

Evolution concept of the atomic structure



Scientists were interested in studying the atomic structure

1 Heisenberg.

2 Pauli.

Schrödinger.

O Bohr.

De Broglie.

1 Einstein.

Planck.

Long time ago man was asking about the nature of matter and its structure ?! While the trials done by the scientists to answer this question across different eras, the concept of the atomic structure is evolved.

In the following, we illustrate the historical evolution for atomic structure concept:

Democritus's idea.

8 Boyle's idea.

Thomson's model of the atom.

1 Bohr's model of the atom.

② Aristotle's idea.

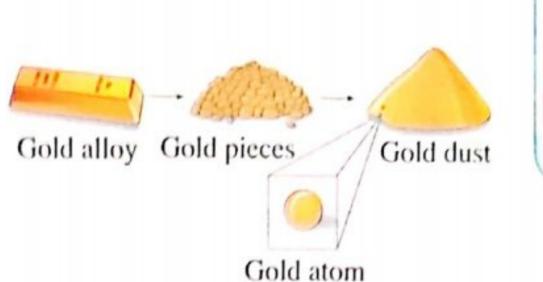
Dalton's model of the atom.

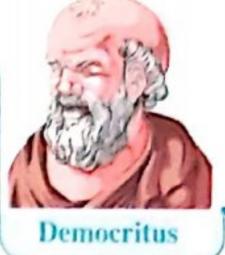
6 Rutherford's model of the atom.

The modern atomic theory.

1 Democritus's (Greek philosopher) idea

He imagined the possibility of dividing any piece of matter to smaller parts, then dividing those parts into smaller particles and so on, until we reach to an undividable fragment, he named it an "atom".





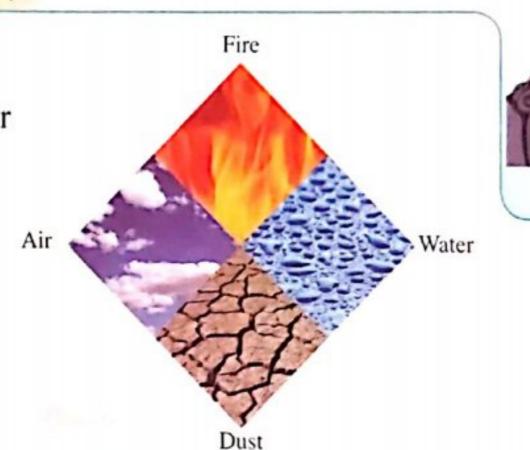
Democritus's atomic concept

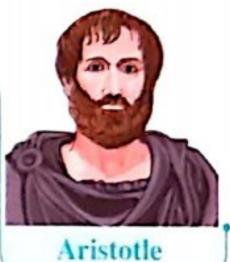
Note

In the Greek language: a means no and tom means divide.

2 Aristotle's idea (4th Century B.C)

- He rejected the concept of the atom and believed that all matter - whatever their nature - are composed of four components, which are water, air, dust and fire.
- It was believed that cheap metals as iron or copper can be changed into precious ones as gold by changing the ratios of these four constituents.



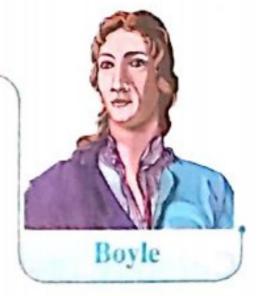


Aristotle's atomic concept

• This illogical idea caused a retard of development in chemistry science for more than thousand years. GR. Because the scientists were busy by changing cheap metals into precious ones.

3 Boyle's idea (1661)

The Irish scientist Boyle refused Aristotle's idea about the nature of substance and gave the first definition of the element.



Element

It is a pure simple substance that can't be changed to simpler forms by the traditional chemical methods.

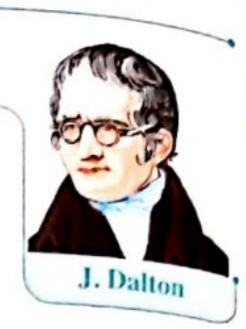


Dalton's model of the atom (1803)

The English scientist John Dalton stated the first theory about the atomic structure.

The main postulates of Dalton's atomic theory:

- 1 The element is composed of very minute particles, which are named atoms.
- 1 The atom is a very minute undividable solid particle.
- The atoms of the same element are similar in the mass, but they are different from the atoms of any other element.
- The compounds are formed by the combination of atoms of different elements in simple numerical ratios.



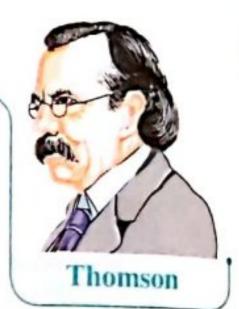




Dalton's atom (solid)

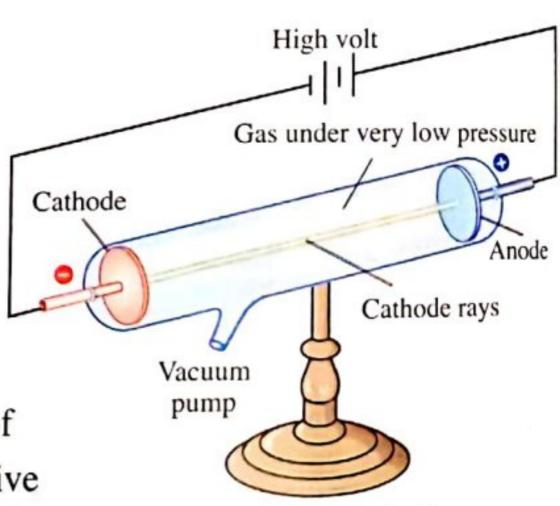
5 Thomson's model of the atom (1897)

The scientist Thomson carried out many experiments on the electric discharge through gases from which he had discovered the cathode rays.



Discovery of cathode rays:

- It was known that gases don't conduct electricity under normal conditions of pressure and temperature.
- However, gases conduct electricity in a discharge tube whose two poles are connected to an electric source of a suitable high potential difference and under a very low pressure.
- If the potential difference between the two poles of the vacuum glass tube exceeds 10000 volts, a stream of invisible rays was emitted from the cathode (the negative pole), causing a fluorescent glow on hitting the tube wall. These rays were named by "cathode rays".



Generation of cathode rays

Cathode rays

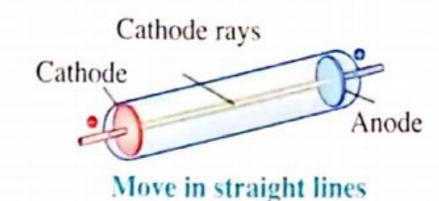
A stream of invisible rays was emitted from cathode, causing a fluorescent glow on hitting the discharge tube wall under a very low pressure and a potential difference is about 10000 volts.

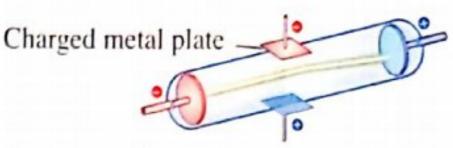
• It was later known that they are composed of minute particles named "electrons".

Properties of cathode rays:

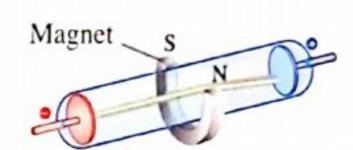
- 1 They consist of very fine negatively charged particles (electrons).
- 1 They move in straight lines.
- 1 They have a thermal effect.
- O They are affected by both electric and magnetic fields.
- They don't differ either in behavior or in nature if the material of the cathode or the used gas is changed, this is a strong evidence that it is a fundamental constituent of any matter.

In the light of the electrical discharge experiment, Thomson suggested a new atomic model for the atom.





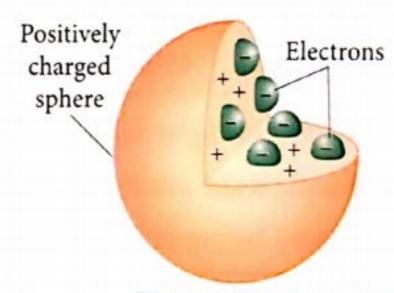
Negatively charged particles affected by electric field



Affected by magnetic field

The postulate of Thomson's model:

He considered the atom as a solid sphere of uniform positive electric charges in which a number of negatively charged electrons is embedded to make the atom electrically neutral.



Thomson's atom (solid)

6 Rutherford's model of the atom (1911)

Rutherford's students Geiger and Marsden performed his famous laboratory experiment.

Rutherford's experiment:

The used tools:

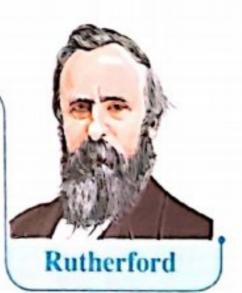
- A deep lead box containing a source of alpha particles (α) inside it.
- A metal sheet covered from the inside with a layer of zinc sulphide ZnS which is used to detect the alpha particles. GR.

Because it glows at the site of collision with alpha particles.

• A very thin gold foil.

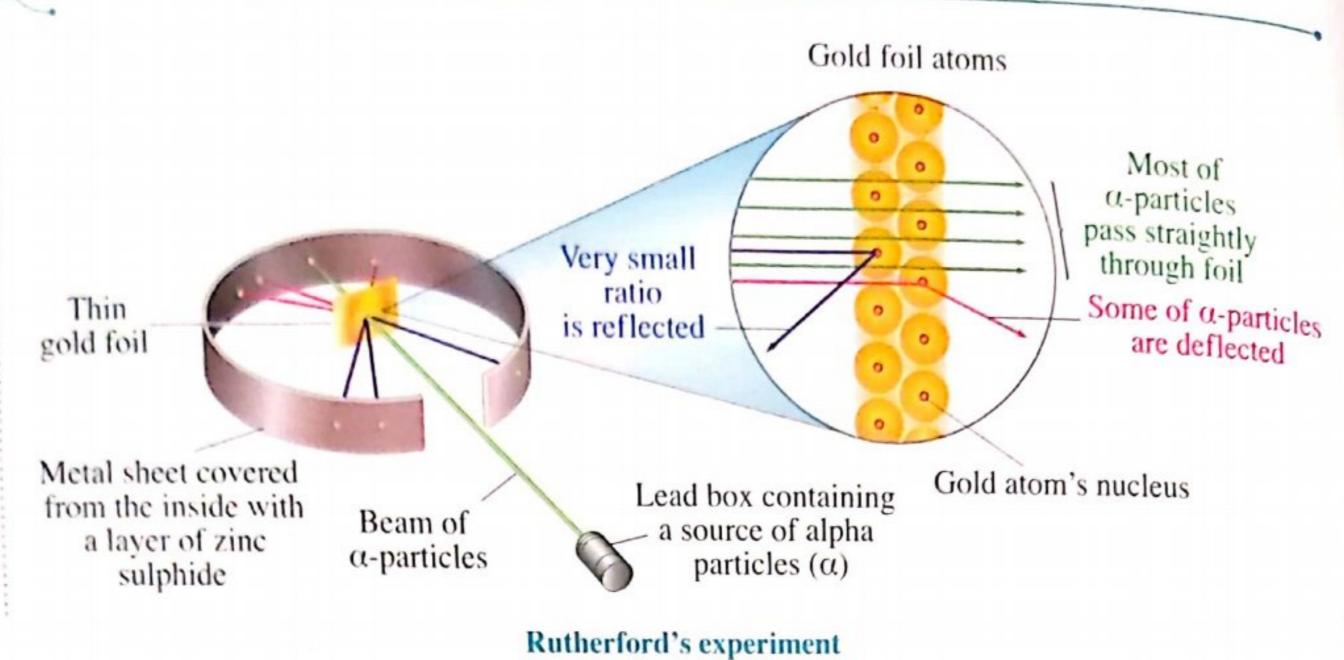
The procedures:

- It was allowed for alpha particles to collide a metal sheet, where it was possible to define the location and number of alpha particles by counting the glows which appeared on the metal sheet.
- 2 A very thin gold foil was placed between the beam of alpha particles and the metal sheet.









Rutherford recorded his observations and reached the following conclusions:

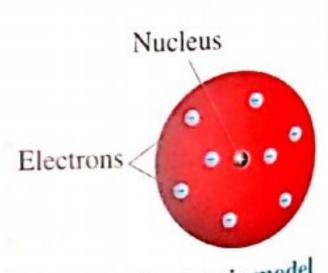
Observations	Conclusions
The most of α-particles penetrated the gold foil and hit the same places in which they appeared before placing the gold foil. A very small ratio of α-particles didn't penetrate the gold foil and reflected back, where some flashes appeared in front of the foil.	Most of the atomic volume is an empty space and the atom is not uniformly dense as proposed by Dalton and Thomson. The atom contains a tiny part of a very high density (was named the nucleus).
Some of α-particles penetrated the foil, but were deflected.	The dense part of the atom (where most of the mass is present) appears to have a similar positive charge to that of α-particles.

On the basis of his experiment and from the experiments of other scientists, Rutherford designed his atomic model as follows:

The postulates of Rutherford's atomic theory:

① Atom:

- It is an extremely small sized particle.
- It has a complicated structure resembles the solar system, since it's composed of a central nucleus (representing the Sun), where the electrons revolve around (representing the planets).



Rutherford's atomic model

Nucleus:

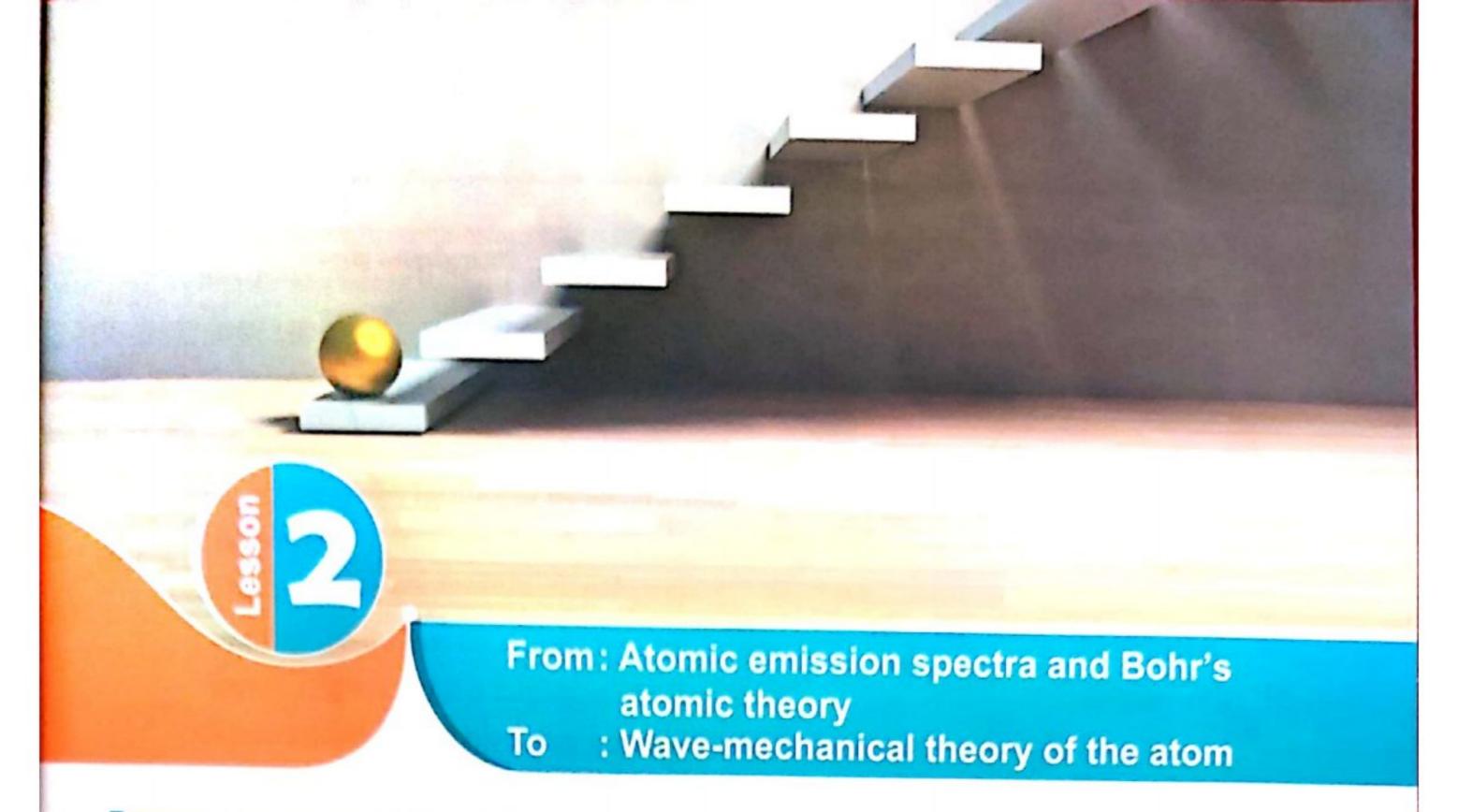
- It is much smaller than the atom and most of the atomic mass is concentrated in it.
- There is a vast space between the nucleus and the orbits of electrons (i.e. the atom is not uniformly dense).
- It is positively charged.

Electrons:

- They have negligible mass compared to that of the nucleus.
- Their charge is negative and equals the nuclear positive charge (i.e. the atom is electrically neutral).
- They travel around the nucleus at a tremendous speed in special orbits, despite of the mutual attraction between them and the nucleus. This attraction force is equal in quantity and opposite in direction to the centrifugal force resulted from the electron revolving around the nucleus.

Give reasons:

- 1 The electron doesn't fall into the nucleus in spite of the attraction force between them. Because the attraction force equals in quantity and opposite in direction to the centrifugal force resulted from the revolving of electron around the nucleus.
- Rutherford's theory had failed to explain the atomic structure. Because it didn't explain the system in which electrons revolve around the nucleus.



Atomic emission spectra:

- On heating atoms of a pure element in gaseous or vapor state to a high temperature or exposing them to a low pressure inside an electrical discharge tube, they emit a radiation called emission spectrum (line spectrum).
- On examining this radiant light by a device called spectroscope, it was found that it is composed of a limited number of restricted colored lines separated by dark areas. So, it is called line spectrum.
- It is worth mentioning that the physicists at that time were not able to explain this phenomenon.

Line spectrum

It is a type of spectrum composed of a small number of restricted colored lines separated by dark areas.

2

Give reason:

The radiant light is named as line spectrum.

Because it is composed of a limited number of restricted colored lines which are separated by dark areas.

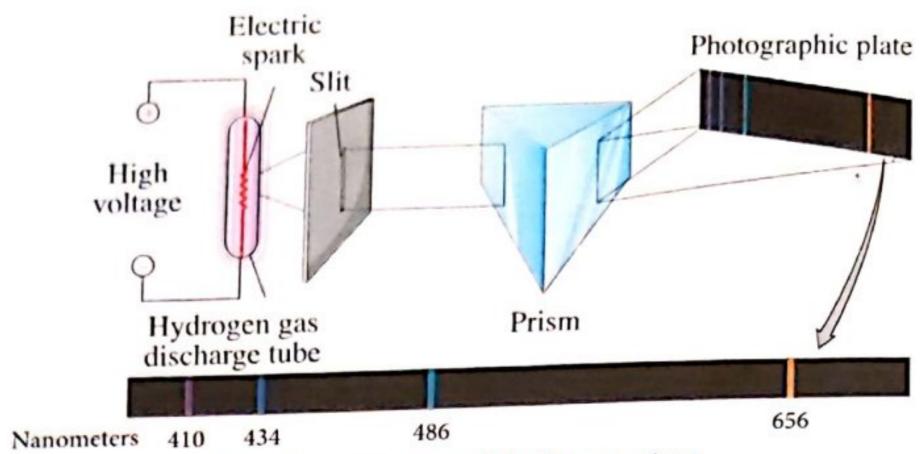
Application

* The line spectrum of hydrogen atom.

The line spectrum of hydrogen atom appears (on examining) as four colored lines separated by dark areas, as the following figure:

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Visible line spectrum of hydrogen atom

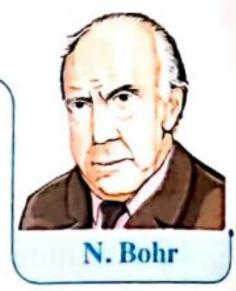
Give reason :

It was found experimentally that the spectral lines are an essential characteristic for each element.

Because there are no two elements have the same spectral lines.

Bohr's atomic model (1913)

The study of atomic spectra is considered the key which solved the puzzle of the atomic structure. That was the work of the Danish scientist Niels Bohr upon which he was rewarded the Nobel Prize in 1922



Bohr's postulates:

A Points that agree with Rutherford's postulates

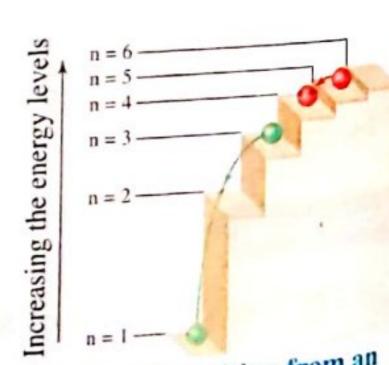
- A positively charged nucleus exists in the center of the atom.
- The number of negative electrons (revolving around the nucleus) equals the number of positive protons inside the nucleus.
- Ouring the revolving of the electron around the nucleus, a centrifugal force arises which is equal to the attraction force of the nucleus on the electron.

Electron Energy level

Bohr's atomic model

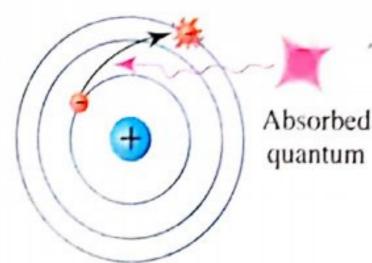
B New postulates

- ① Electrons orbit the nucleus in a rapid movement without emission or absorption of any amount of energy and the atom in this case named stable atom.
- Electrons orbit the nucleus in definite allowed energy levels. They can't be found at intermediate distances, at which electron moves from an energy level to another one via a complete jumping.

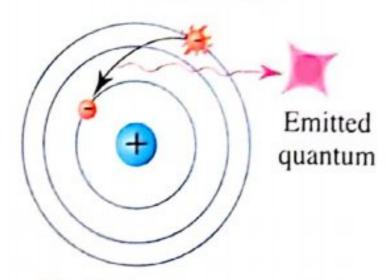


Electron transition from an energy level to another one takes place via a complete jumping

- Each electron in the atom has a definite amount of energy depending on the distance between its energy level and the nucleus, the energy of any level increases as its radius increases. Each energy level is expressed by a whole number called the principal quantum number (n).
- When the electron acquires a quantity of energy known as quantum by heating or by electric discharge, the electron jumps temporarily to a higher energy level. This is in case that the absorbed quantum of energy is equal to the difference in energies between the two levels, and the atom is known as "excited atom". Since the electron in the excited atom is unstable, it returns back to its original level with emission of the same quantum of energy (emission spectrum) in the form of radiant light that appears in the form of a characteristic spectral line of a certain wavelength and frequency.



Excited atom



Excited atom returns back to its original stable state

Quantum

It is the amount of energy absorbed or emitted, when an electron is transferred (jumps) from an energy level to another.

Excited atom

It is an atom acquired an amount of energy by heating or by electric discharge.

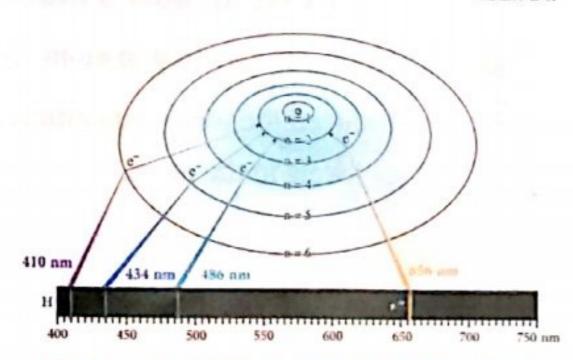
The multitude of atoms absorb different amounts of energy, then radiate their energies producing spectral lines. These spectral lines correspond to the energy levels from which their electrons are transmitted back to the ground state.

For illustration only

The opposite figure which is representing the spectral line of the hydrogen atom doesn't represent the electron transferring from:

- The different energy levels to the first energy level, because the wavelength of the emitted ray from the excited electron is located in the invisible region of the ultraviolet rays.
- The seventh energy level to the second energy level, because the wavelength of the emitted ray from the excited electron is located in the invisible region of the infrared rays.





The visible spectral line of hydrogen atom consists of four colored lines.



N.B

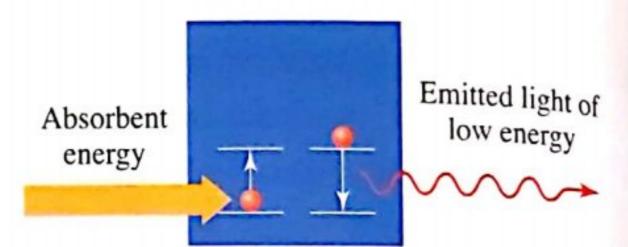
- 1 The quantum of energy required to transfer an electron between the different energy levels is not equal.
- One quantum is the energy difference between the two energy levels.
- 1 It is impossible for an electron to move from its energy level to another, if the energy absorbed or emitted is less than one quantum.
 - (i.e. there is no a half quantum for instance)

Give reasons:

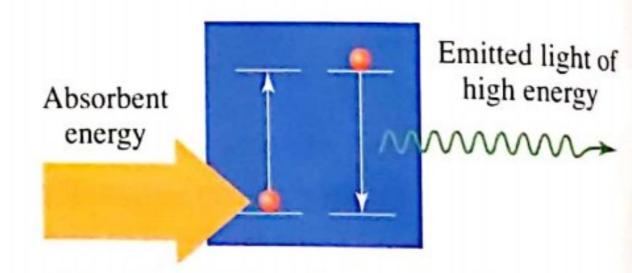
- The quantum of energy required to transfer an electron between the different energy levels is not equal.

 Because the distance and the difference in energy between them are not equal.
- The quantum of energy required to transfer an electron from an energy level to another decreases as we go further from the nucleus.

Because the energy gap decreases, as we go further from the nucleus.



Electron transfers between two levels close in energy



Electron transfers between two levels of a big difference in energy

The advantages and inadequacies of Bohr's atomic model

Despite of the great effort of Bohr to construct his atomic model, the quantitative calculations of his theory didn't agree with all the experimental results.

Advantages (success) of Bohr's atomic model:

- 1 It explained the hydrogen atom spectrum.
- It introduced the idea of quantized energy to determine the electron energy in different energy levels in the atom.

Inadequacies of Bohr's atomic model:

The most important defects of Bohr's theory were the following:

It failed to explain the spectrum of any other element, except hydrogen atom. GR. As it is considered the simplest electronic system which contains one electron only, even that of the helium atom which contains only 2 electrons.

- 1 It considered the electron as a negative charged particle only and ignored its wave properties.
- 1 It postulated that it is possible to determine precisely both of the location and speed of an electron at the same time, but in fact this is experimentally impossible.
- It described the electron as a particle moving in a circular planar orbit, this means that hydrogen atom is planar. Later on it was confirmed that the hydrogen atom has a spherical shape (three dimensional coordinates).

8 The principle of modern atomic theory (modification of Bohr's model):

The modern atomic theory is based on some essential modifications of Bohr's model.

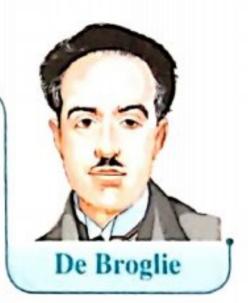
The most important modifications are the following:

- 1 The dual nature of electron.
- 2 The Heisenberg uncertainty principle.
- 1 The wave-mechanical theory of the atom.

1 The dual nature of electron

All the previously mentioned theories considered the electron just as a minute negatively charged particle. However, all experimental data showed that the electron has a dual nature. GR.

As it is a material particle which also has wave properties.



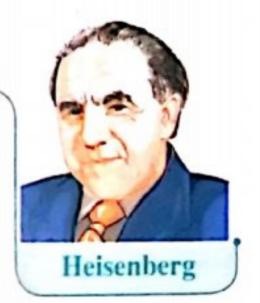
The dual nature of electron

The electron is a material particle which has wave properties.



The Heisenberg uncertainty principle

Bohr's theory postulated that it is possible to determine both of the location and velocity of the electron precisely at the same time, but by applying the principles of quantum mechanics, Heisenberg concluded that "the determination of both the velocity and position of an electron at the same time is practically impossible. So, to speak in terms of "probability" seems to be more precise".



This is because the electron wave motion doesn't have a certain location.



Heisenberg uncertainty principle

The determination of both the velocity and position of an electron at the same time is practically impossible and this is subjected to the laws of probability.

3 The wave-mechanical theory of the atom

The Austrian scientist Schrödinger (1926) applied the idea of Planck, Einstein, De Broglie and Heisenberg and could to:

- Establish the wave-mechanical theory of the atom.
- Derive a wave equation that could describe the electron wave motion in the atom.

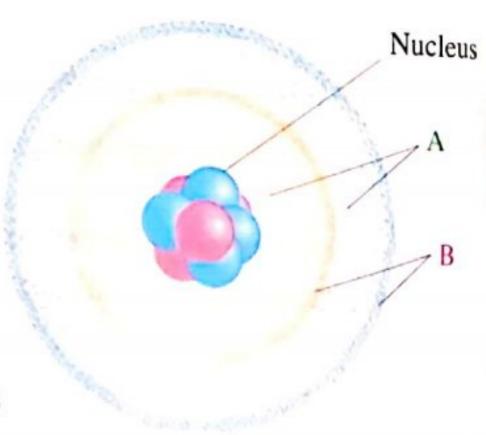


- ① Determine the allowed energy levels.
- ② Define the regions of space around the nucleus, where it is most probable to find the electron in each energy level.
- The wave-mechanical theory changed our concept about the movement of electron, where instead of speaking about the fixed circular orbits as being completely forbidden for electrons, the concept of "the electron cloud" (region A) is used to express the region of space around the nucleus.

Electron cloud

It is the region of space around the nucleus, in which the electron probable exists in all directions and distances (dimensions).

• There are regions inside the electron cloud in which probability of finding the electron increases, each of them is termed by "the orbital" (region B).



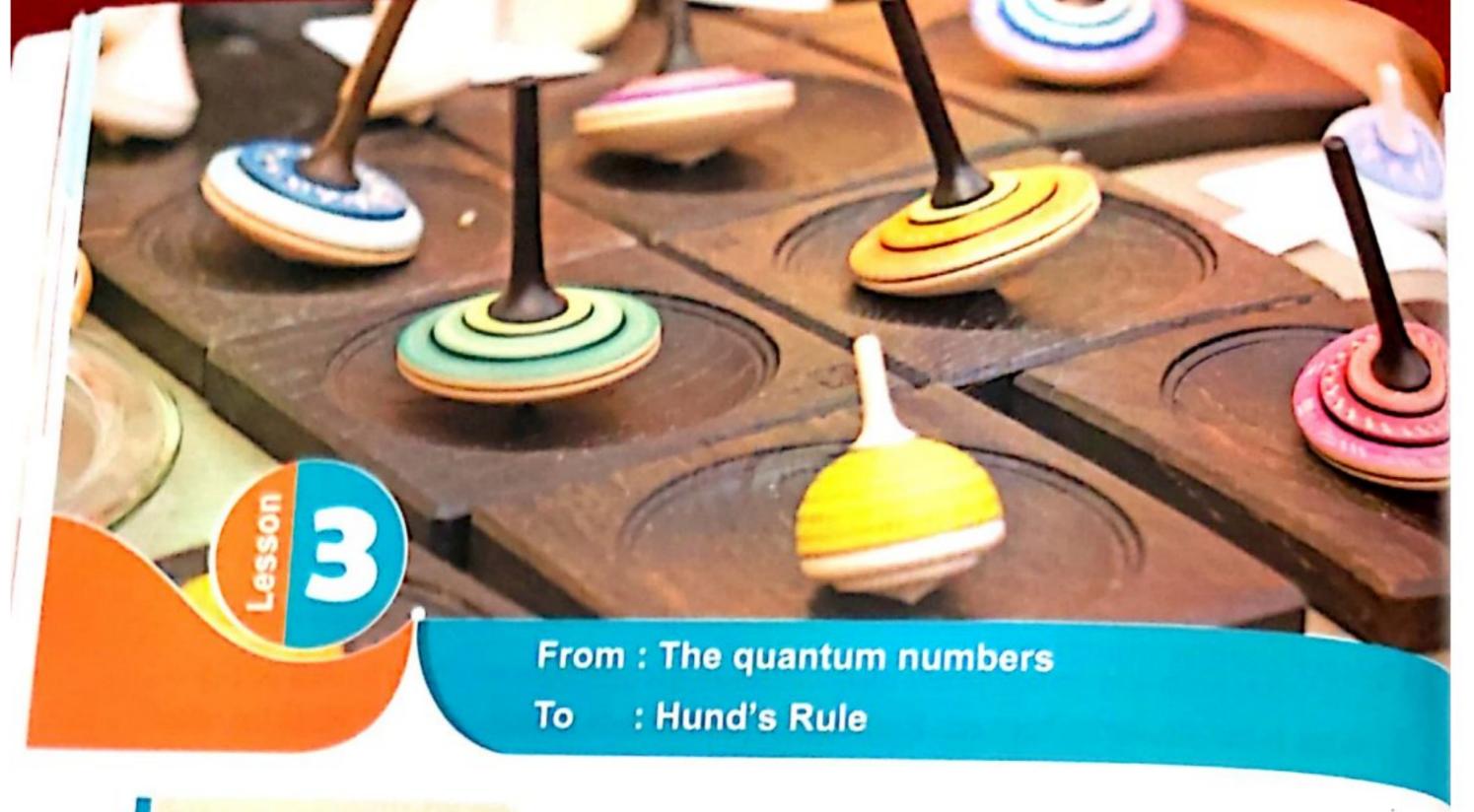
Schrödinger

Electron cloud and orbital

Orbital

It is the region within the electron cloud of high probability of finding the electron.

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Quantum numbers

The mathematical solution of Schrödinger's equation introduced four numbers that were called quantum numbers.

To determine the energy of an electron in multi-electron atoms, we should know the four quantum numbers which describe it, these four quantum numbers are :

- The principal quantum number (n):
 - It describes the distance of the electron from the nucleus.
- 2 The subsidiary quantum number (l):

It describes the shapes of electron cloud in the sublevels.

- The magnetic quantum number (m_l):
 - It describes the shape and number of the orbital in which the electron exists.
- The spin quantum number (m_s) :

It describes the spin of the electron.

- The principal quantum number (n):
- (a) Bohr had used this number in explaining the spectrum of hydrogen atom, it is given the symbol (n) and it is used to define the following:
 - 1 The order of principal energy levels or electron shells. Their number in the heaviest known atom in its ground state is seven.
 - The number of electrons (e) required to fill a given energy level which equals the formula $2n^2$ (i.e. two times the square of the shell number). 28

(n)	The number of electrons required to fill the energy level (2n2)
1st shell (K)	$(2 \times 1^2) = 2$ electrons
2 nd shell (L)	$(2 \times 2^2) = 8$ electrons
3 rd shell (M)	
4 th shell (N)	$(2 \times 4^2) = 32$ electrons

Give reason:

The rule 2n² isn't applied to the energy levels higher than the fourth level.

Because the atom becomes unstable, if the number of electrons exceeds 32 electrons in any level.

(b) The principal quantum number has whole number values 1, 2, 3, 4, etc, excluding zero. Each value is expressed by an alphabetical letter that represents a principal energy level as shown in the following table:

Energy of levels increases from K to Q

The subsidiary quantum number (()

- (a) It is given the symbol (l). It determines the number of sublevels in each principal energy level.
- (b) Each principal energy level consists of a number of energy sublevels equals to its principal quantum number.
- (c) The energy sublevels take the symbols and values as shown in the following table:

Symbols of sublevels	S	p	d	f
Subsidiary quantum number (l) values [0: (n-1)]	0	1	2	3



The following table represents the relation between the principal quantum number (n) The following table representations of subsidiary quantum number (l), where

Principal energy levels	Principal quantum number (n)	Sublevels	Values of the sublevels
K	1		O
L	2 —	2s	0
		2p	1
M	3——	3s	0
		3p	1
		3d	2
		4s	0
N	4	4p	1
		4d	2
observed that there		4f	3

^{*} It is observed that there is a small difference in the energy of the sublevels in each

* They can be arranged according to increasing their energy as the following order:

$$s$$

Examples

1 What are the probable (l) values when n = 3?

Solution

- : Each principal energy level consists of a number of sublevels which equals its
- \therefore No. of sublevels = 3
- :. The probable (ℓ) values range between [0:(n-1)]=[0:(3-1)]=0, 1, 2
- 2 Mention the sublevels which exist in an atom of a certain element, knowing that its last

Solution

The principal energy levels exist in this atom are K, L

Principal energy level	Values of the principal quantum number (n)	Values of the subsidiary quantum no. (ℓ) [0 : (n – 1)]	Energy Sublevels
K	1		1s
L	2		2s, 2p

- :. The sublevels present in this atom: 1s, 2s, 2p
- The magnetic quantum number (m_l)
- (a) It determines the number of orbitals within a certain energy sublevel from the relation: (2l + 1).
- (b) It determines the spatial orientation (orientation in space) of orbitals.
- (c) It is represented by whole number values (odd) ranging between (-l, ..., 0, ..., +l). The following table shows the relation between (l) values and the probable values of the magnetic quantum number (m_{ℓ}) for the first four energy levels of an atom.

Values of the principal quantum number (n)	Values of the subsidiary quantum number (l) [0:(n-1)]	Symbols of energy sublevels	Values of the magnetic quantum number (m_l) $(-l,, 0,, +l)$	Number of the sublevel orbitals (2 \(\ell + 1 \)	Number of the principal level orbitals (n²)
1	0	Is	0	1	1
2	0	2s	0	1	
2	1	2 <i>p</i>	-1,0,+1	3	4
	0	3s	0	1	
3	1	3р	-1,0,+1	3	9
	2	3d	_2, _1, _0, _+1, _+2	5	
	0	4s	0	1	
4	1	4p	-1,0,+1	3	16
•	2	4d	-2, -1, 0, +1, +2	5	16
	3	4f	-3, -2, -1, 0, +1, +2, +3	7	

Chapter

(d) The orbitals of the same sublevel are equal in energy, but differ in direction and shape in

space as shown in the following table:

Sublevels	Number	Shape in space (electron density)	Figure
S	1	Spherical symmetrical shape around the nucleus.	Orbital 1s Orbital 2s
		 Each orbital takes the form of two pears meeting head to head (dumb-bell shaped) at a point of zero electron density (node). 	$\frac{y}{z}$
p	3	 The three orbitals whose axes take the three spatial orientations, thus they are designated as p_x, p_y and p_z Each orbital is perpendicular to the other two orbitals. 	Orbital p_x Orbital p_y Orbital p_z
d	5		
f	7	Comp	licated shapes

Any orbital can't be occupied by more than two electrons.



Give reason:

The p-sublevel is completely filled with $6\,\mathrm{e}^-$, while the d-sublevel is completely filled with $10\,\mathrm{e}^-$

Because the p-sublevel contains 3 orbitals, while the d-sublevel contains 5 orbitals and each orbital is filled with $2\,\mathrm{e}^-$

Examples

1) What are the probable (m_l) values when (l = 2)?

Solution

- : The probable (m_l) values range between -l, ..., 0, ..., +l
- \therefore The probable (m_l) values: -2, -1, 0, +1, +2

Which of the following probabilities of the quantum numbers of a certain electron includes a mistake? Giving reason.

(a)
$$n = 3$$
, $l = 2$, $m_l = -1$

(b)
$$n = 4$$
, $l = 3$, $m_l = -2$

(c)
$$n = 1$$
, $l = 1$, $m_l = +1$

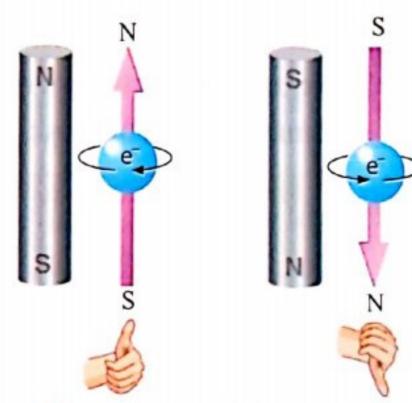
Solution

The choice (c), because when (n = 1) the probable ℓ and m_{ℓ} values are (0).

The spin quantum number (m_s)

Since any orbital can't be occupied by more than two electrons, each electron spins on its own axis during its orbit around the nucleus, like the spinning of the Earth on its own axis during its rotation around the Sun.

- * The spin quantum number determines the type of spin motion of the electron around its axis in the orbital, which is either:
 - Clockwise ($\frac{1}{1}$) with m_s value equals $(+\frac{1}{2})$.
 - Anticlockwise (\downarrow) with m_s value equals $(-\frac{1}{2})$.



The two cases of electron spin

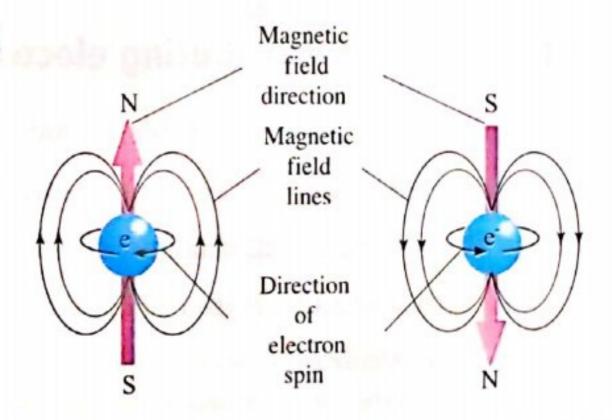
Orbitals have three different possibilities depending on the number of electrons located in them as follows:

- Empty orbital.
- Half-filled orbital contains one electron.
- Completely-filled orbital contains 2 pairing electrons that have opposite spins and called spin paired state.

Give reason :

Although the two electrons of the same orbital carry the same negative charge, they don't repel with each other.

Because the magnetic field arises from the spinning of one electron is in a direction opposing the direction of the other magnetic field arising from the spinning of the other electron and that decreases the repulsive force between the two electrons.



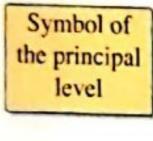
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- Summary of the relationship between the principal energy level, sublevels and orbitals,
- **1** Each principal energy level:
 - (a) Consists of a number of sublevels equals its number (n = no. of ℓ values).
 - (b) Consists of a number of orbitals equals square the number of the level (n²).
 - (c) The number of electrons occupying it, equals two times the square of the level number (2n²)
- **2** Each sublevel consists of a number of orbitals which equals (2 l + 1).
- **Solution** Each orbital occupied by 2 electrons:

Sublevel	s	p	d	$\int f$
Number of orbitals	1	3	5	7
Electron capacity	2	6	10	14

The quantum numbers of the electrons occupying the first three energy levels are summarized as follows:



The principal quantum number (n)

Sublevels in each principal level

35

2s

The sublevel quantum number (1)

No. of orbitals in each sublevel (2l+1)

No. of electrons filling each sublevel

No. of electrons filling each principal quantum number (2n2)

M

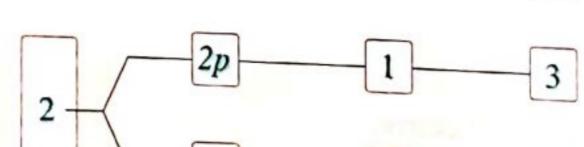
Increasing the energy and volum



$$5 \times 2 = 10 e^{-}$$

 $3 \times 2 = 6e^{-}$

 $1 \times 2 = 2e^{-}$



$$3 \times 2 = 6 e^{-}$$

$$1 \times 2 = 2e^{-}$$

 $1 \times 2 = 2e^{-}$

Principles of distributing electrons

There are some important rules, which must be considered in distributing electrons in the atom. These rules are:

- 1 Pauli's exclusion principle.
- Aufbau (building-up) principle.
- 3 Hund's rule.

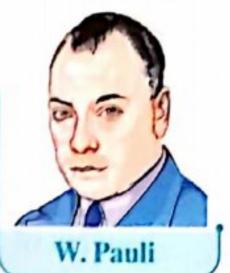


1 P

Pauli's exclusion principle

Pauli's exclusion principle

It is impossible for two electrons in the same atom to have the same four quantum numbers.



Application

The corresponding table shows the two electrons of the (3s) sublevel which are similar in the values of the quantum numbers (n, l, m_l) , but they are different in the two values of the spin quantum number (m_s) .

The four quantum no.	n	(1	m_l	m _s
The first electron	3	0	0	$+\frac{1}{2}$ $-\frac{1}{2}$
The second electron	3	0	0	$-\frac{1}{2} + \frac{1}{2}$

Example

Write the possible values of the four quantum number for each of the following:

- (a) An electron in 2p-sublevel.
- (b) The first electron in 4d-sublevel.
- (c) The second electron in1s-sublevel.

The quantum numbers		n	l	$m_l = -l,, 0,, +l$	$m_s = \pm \frac{1}{2}$
The possible values	(a)	2	1	-1 or 0 or +1	$+\frac{1}{2}$ or $-\frac{1}{2}$
of quantum numbers	(b)	4	2	-2	+ 1/2
or quantum mambers	(c)	1	0	0	$-\frac{1}{2}$

Note

When (np) sublevel contains one electron, it is not necessary to be :

- $(m_l = -1)$, but it may be equal 0 or +1
- $(m_s = +\frac{1}{2})$, but it may be equal $-\frac{1}{2}$

(3) (2p) 4 (3) (3p) (3d) - 6 (4) (4p) (4d) (4f) - 8 (5) (5p) (5d) (5f) (6) (6p) (6d)

2 Aufbau (building-up) principle

Aufbau (building-up) principle

Electrons occupy the sublevels in the order of increasing their energy, the lowest energy sublevels are filled firstly.

* The sublevels of the same principal energy level differ slightly from each other in energy.

A simple way of the order of filling the energy sublevels according to the direction of the arrows



- * Arrangement of sublevels according to their energy depends on :
 - Sum of (n + l).

Ex. Energy of 4s sublevel is lower than that of 3d sublevel. (CR.)

Because sum of (n + l) of 4s sublevel is less than that of 3d sublevel.

• Order of the principal energy level.

"In case of equality of sum (n + l) values for two sublevels".

Ex. Energy of 3p sublevel is lower than that of 4s sublevel. GR.

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	- 2	5	dir.	2
1	200	1	Non	6
	-	7	Aus	9

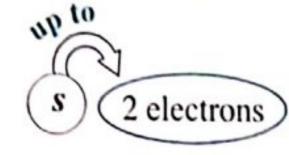
Sublevels	Sum of (n+b)
3р	3 + 1 = 4
4s	4 + 0 = 4
3d	3 + 2 = 5

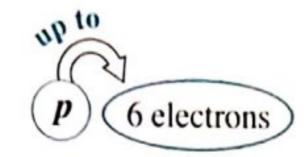
Because (n) value of 3p sublevel is lower than that of 4s sublevel.

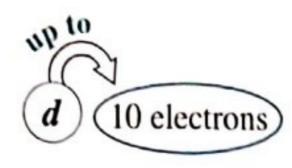
* The sequence of energy sublevels is arranged ascendingly according to their energy follows the order:

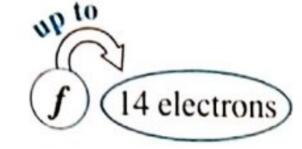
1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d < 7p

* Filling the energy sublevels:









* The electron configuration for one of the energy levels can be expressed as the following:

Number of electrons in the orbitals of sublevel

Principal energy level (n)

Energy sublevel

Example

Write the electron configuration for the following elements, according to building-up principle:

Solution

$$11$$
Na: $1s^2$, $2s^2$, $2p^6$, $3s^1$

$$20$$
Ca: $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^2$

$$_{30}$$
Zn: $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^2$, $3d^{10}$

$$_{19}$$
K : $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^1$

$$26^{\text{Fe}}: 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^6$$

Hund's rule

Hund's rule

No electron pairing takes place in a given sublevel until each orbital contains one electron.



• Rules of filling the energy sublevels with electrons, according to Hund's rule :

Rule	Application
The orbitals of the same sublevel are equal in their energy.	The three 2p orbitals are equal in energy 3d The five 3d orbitals are equal in energy
The orbitals of the same sublevels are filled by the unpaired electrons firstly. The spin of single electron in the same direction gives the atom more stability.	$p^{1} \uparrow \qquad p^{2} \uparrow \uparrow \qquad p^{3} \uparrow \uparrow \uparrow$ $ \uparrow^{N} \downarrow \downarrow \qquad \downarrow^{1} \downarrow \qquad \downarrow^{1} \downarrow \qquad \downarrow^{1} \downarrow \qquad \downarrow^{1} \downarrow$ $ \uparrow^{N} \downarrow \downarrow \qquad \downarrow^{1} \downarrow \qquad \downarrow^{1} \downarrow \qquad \downarrow^{1} \downarrow \qquad \downarrow^{1} \downarrow$ $ \uparrow^{N} \downarrow \downarrow \qquad \downarrow^{1} \downarrow \qquad \downarrow^{1} \downarrow \qquad \downarrow^{1} \downarrow \qquad \downarrow^{1} \downarrow$ $ \uparrow^{N} \downarrow \downarrow \qquad \downarrow^{1} \downarrow \qquad \downarrow^{1} \downarrow \qquad \downarrow^{1} \downarrow \qquad \downarrow^{1} \downarrow$ $ \uparrow^{N} \downarrow \downarrow \qquad \downarrow^{1} \downarrow \qquad \downarrow^{1} \downarrow \qquad \downarrow^{1} \downarrow \qquad \downarrow^{1} \downarrow$ $ \uparrow^{N} \downarrow \downarrow \qquad \downarrow^{1} \downarrow \qquad \downarrow^{1} \downarrow \qquad \downarrow^{1} \downarrow \qquad \downarrow^{1} \downarrow$ $ \uparrow^{N} \downarrow \downarrow \qquad \downarrow^{1} \downarrow \qquad \downarrow^{1} \downarrow \qquad \downarrow^{1} \downarrow \qquad \downarrow^{1} \downarrow$ $ \uparrow^{N} \downarrow \downarrow \qquad \downarrow^{1} \downarrow \qquad \downarrow^{1} \downarrow \qquad \downarrow^{1} \downarrow \qquad \downarrow^{1} \downarrow$ $ \uparrow^{N} \downarrow \downarrow \qquad \downarrow^{N} \downarrow \qquad \downarrow^{N} \downarrow \qquad \downarrow^{N} \downarrow$
When the two electrons are paired in one orbital, they have opposite spins. GR. To decrease the repulsive force between them. Then the two electrons are in a spin-paired state.	$_{2}$ He $\uparrow \uparrow$ $_{1}s^{2}$ $_{2}$ He $\downarrow \downarrow$ $_{1}s^{2}$
Electrons pairing takes place in the orbitals of the same sublevel after occupying all orbitals by the unpaired electrons.	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$
The electron prefers to be paired with another electron in one orbital of the same sublevel rather than being transferred to a higher energy sublevel.	$2s^{1} \uparrow \qquad 2s^{2} \uparrow \downarrow \qquad 1s^{2} \downarrow \downarrow \qquad 1s$

Give reasons:

The spin of single electrons in the same sublevel orbitals is in the same direction. Because this state gives the atom more stability.

The electron prefers to occupy an orbital alone in the same sublevel rather than pairing with another one in the same orbital.

Because when two electrons are paired in one orbital, (in spite of their opposite spins), there must be a repulsive force that decreases the stability of the atom (increasing in its energy).

The electron prefers pairing with another one in orbital in the same sublevel rather than transferring to the higher energy sublevel.

Because the required energy to overcome the repulsive force between the two paired electrons is less than that is required for transferring the electron to a higher sublevel.

Application

The electron configuration of some elements according to building-up principle and Hund's rule:

Element	Atomic number	Electron configuration according to building-up principle	Electron configuration according to Hund's rule
Hydrogen 1H	1	$1s^1$	$1s^{I}$
Helium ₂ He	2	$1s^2$	$1s^2$
Lithium ₃ Li	3	$1s^2$, $2s^1$	$2s^{1}$
Boron ₅ B	5	$1s^2, 2s^2, 2p^1$	$2p^{l} \uparrow$ $2s^{2} \uparrow \downarrow$ $1s^{2} \uparrow \downarrow$
Carbon 6C	6	$1s^2, 2s^2, 2p^2$	$1s^{2}, 2s^{2}, 2p_{X}^{I}$ $2p^{2} \uparrow \uparrow \uparrow$ $2s^{2} \downarrow \downarrow$ $1s^{2} \downarrow \downarrow$ $1s^{2}, 2s^{2}, 2p_{X}^{I}, 2p_{Y}^{I}$
Nitrogen 7N	7	$1s^2, 2s^2, 2p^3$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$

Fluorine ₉ F	9	$1s^2, 2s^2, 2p^5$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$
Neon 10 ^{Ne}	10	$1s^2, 2s^2, 2p^6$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$

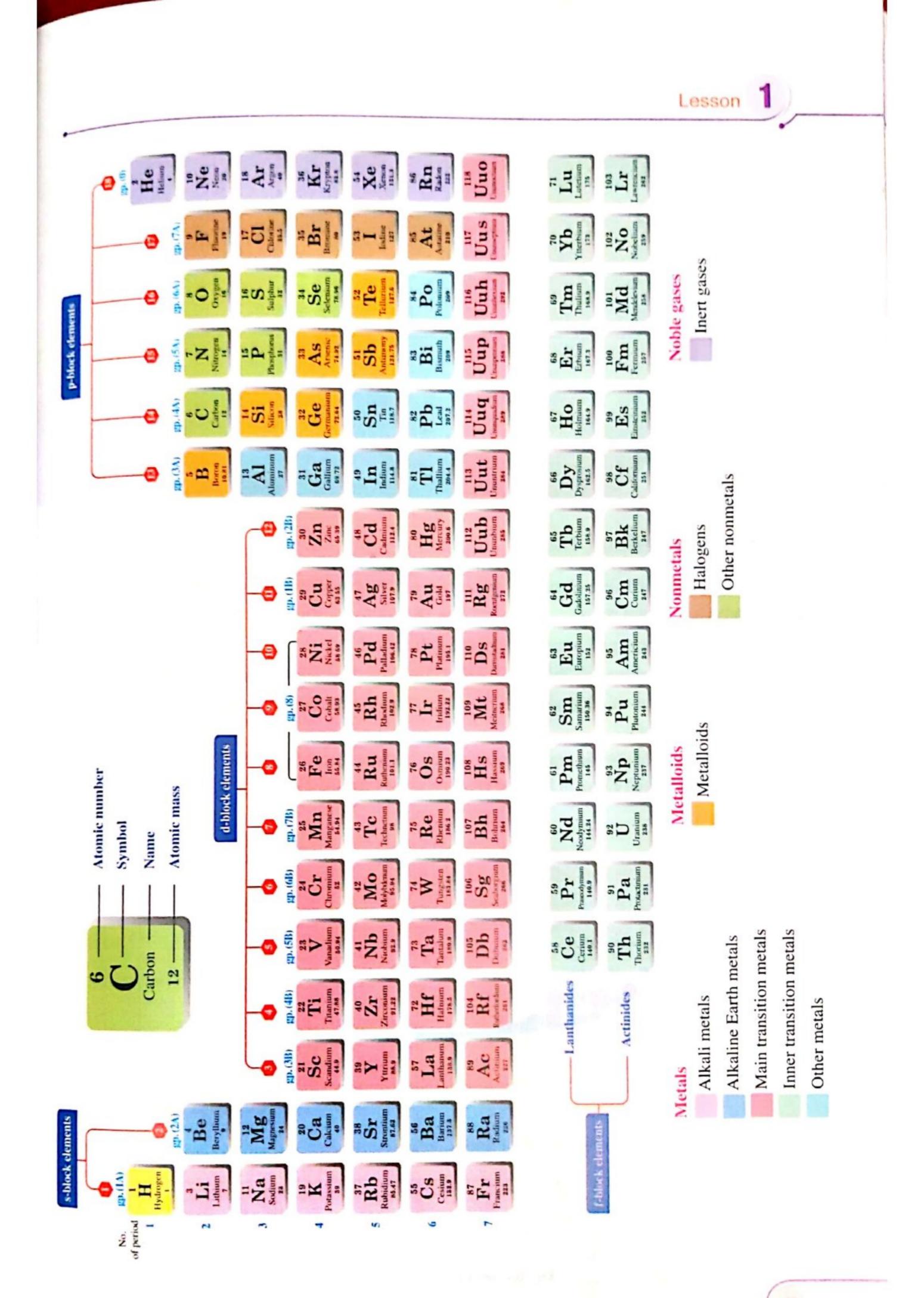
Example

Predict the atomic number for each of the following elements:

- 1 An element whose electronic configuration is $1s^2$, $2s^2$, $2p^3$
- 2 An element whose principal energy level (n = 3) contains 3 electrons.
- An element whose last 3s-sublevel is half-filled with electrons.

Solution

- The electronic configuration: $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^1$
 - \therefore The atomic number = 13
- 13 The electronic configuration: $1s^2$, $2s^2$, $2p^6$, $3s^1$
 - \therefore The atomic number = 11





The modern periodic table

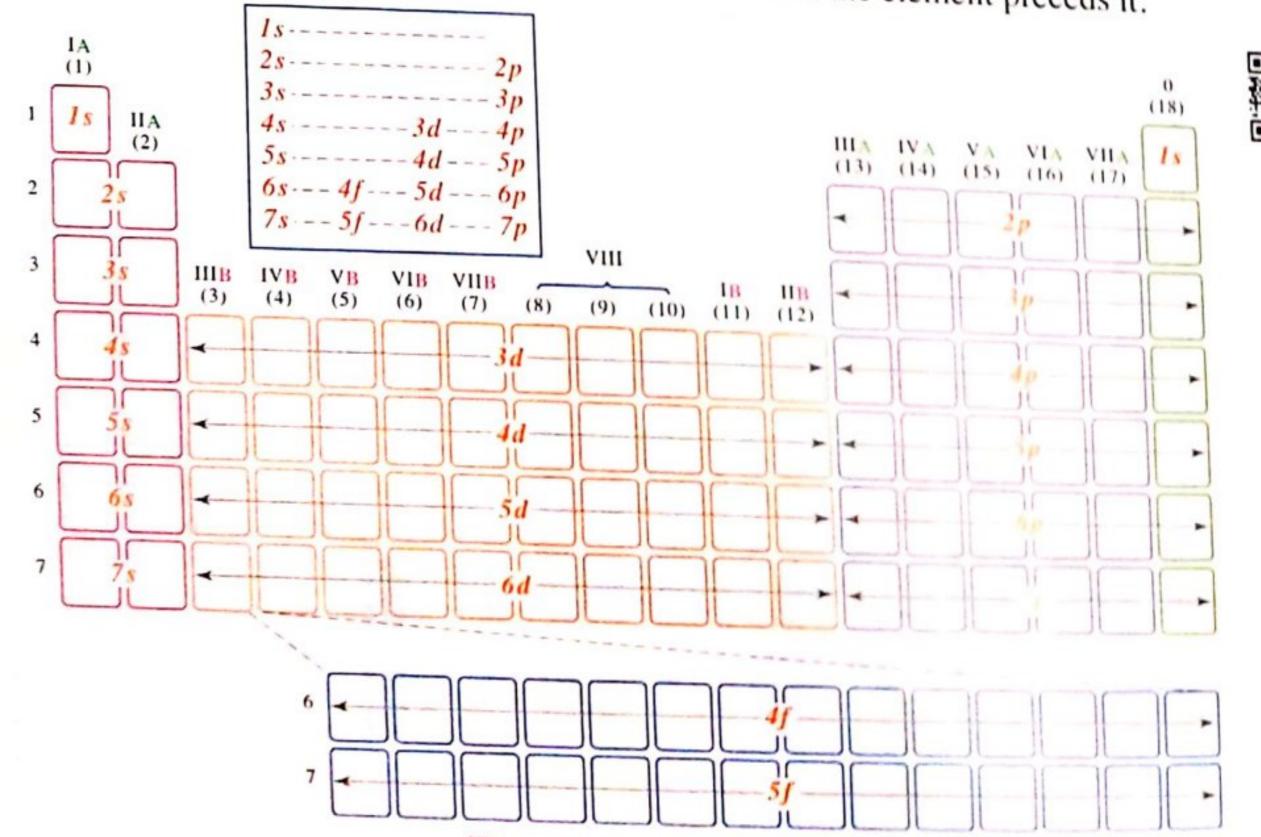
The modern periodic table consists - as shown on the corresponding page - of :

7 periods (horizontal rows).

• 18 groups (vertical columns).

The elements are arranged ascendingly according to :

- Their atomic numbers :
 - The atomic number of each element increases than the element preceds it in the same period by whole one.
- The way to fill their atomic energy sublevels by electrons according to the Aufbau (Building-up) principle, where each element has one electron more than the element preceds it.



The modern periodic table

Each period begins by filling a new energy level with one electron, then filling the atomic energy sublevels lying in the same period successively, until we reach the last element in the period which is a noble gas that has completely filled energy levels.

The elements of the same vertical group are:

- Identical in the electronic composition of the highest (outermost) energy level.
- Different in the principal quantum number (n).

Give reason:

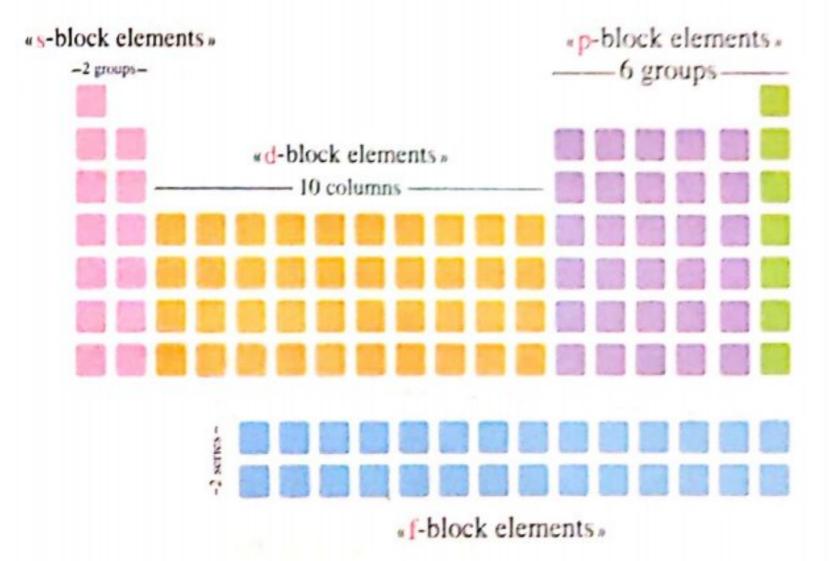
Both of sodium 11Na and potassium 19K have similar properties. Because they are identical in the electronic composition of the highest (outermost) energy level (ns1).

* The modern periodic table consists of 118 elements distributed in seven horizontal periods, as follows:

Period	First	Second	Third	Fourth	Fifth	Sixth	Seventh
Number of elements	2	8	8	18	18	32	32

The elements blocks of the modern periodic table

- The table is divided into four main blocks, these blocks are :
- 1 s-block.
- 2 p-block.
- d-block.
- Of-block.

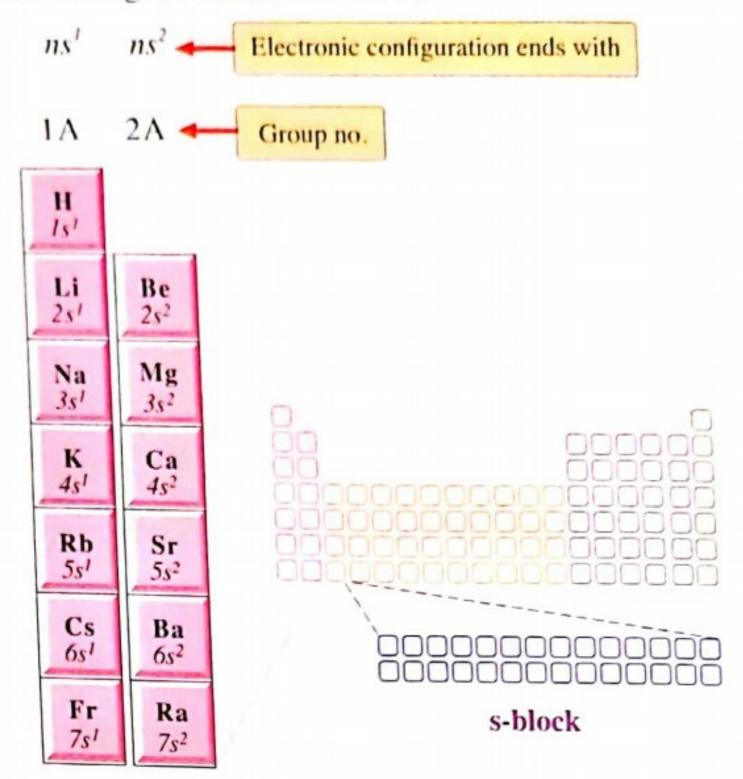


s-block elements

- They are placed in the left hand block of the table.
- The s-block contains the elements whose outermost electrons occupy the "s" sublevel.
- The s-block consists of two groups of elements, they are:



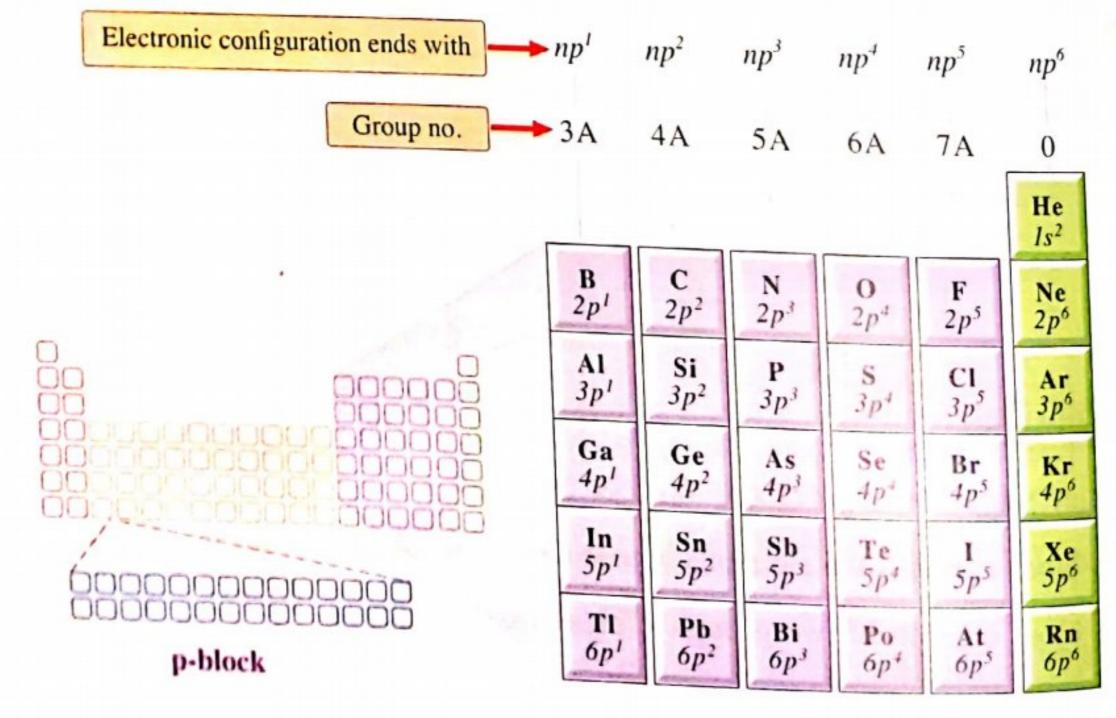
- 1A whose electronic configuration ends with ns1
- 2A whose electronic configuration ends with ns²



Where "n" is the number of the outer energy level and the number of period at the same time.

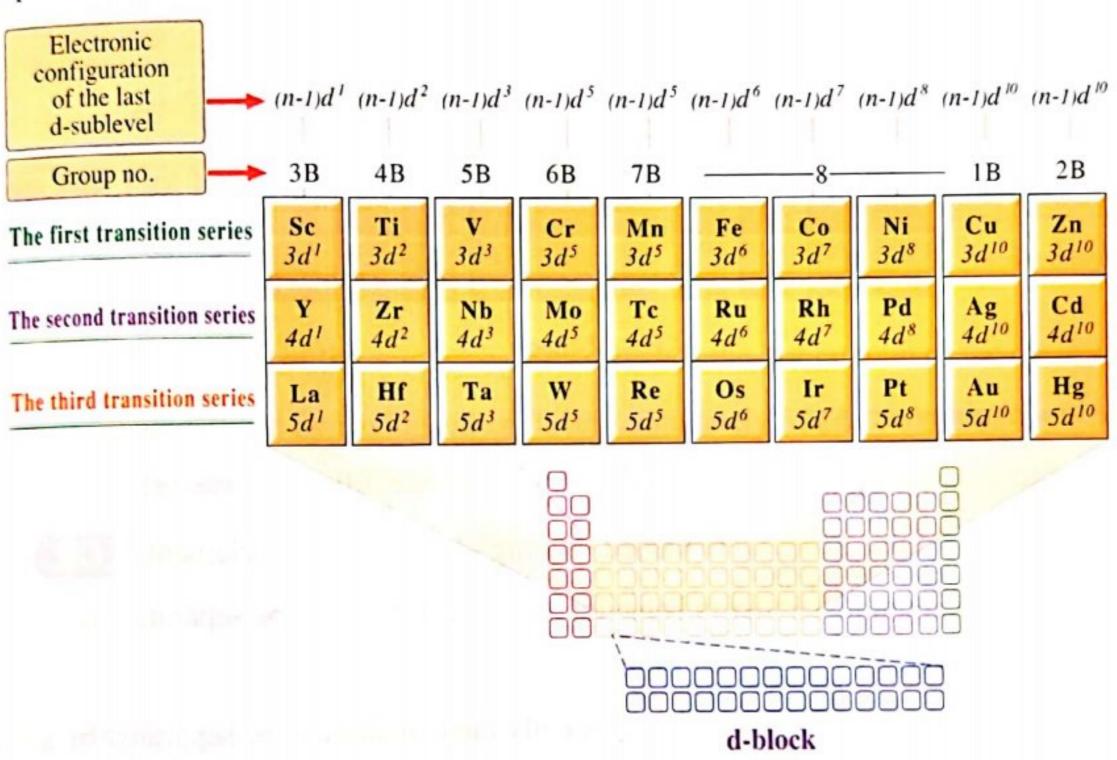
2 p-block elements

- They occupy the right hand block of the table.
- The p-block contains the elements whose outermost electrons occupy the "p" sublevel, except helium.
- The p-block consists of six groups, characterized by symbol "A" except "zero group", as follows:



3 d-block elements

- They occupy the middle block of the table.
- The d-block contains the elements with the outermost electrons occupy the "d" sublevel.
- The d-block consists of "10" vertical columns representing "8" groups which are characterized by the symbol "B" except eighth group which consists of "3" vertical columns.
- The d-block elements are classified according to the number of the outer energy level and the period number into three series which are:



1 The first transition series:

- It includes the elements in which the "3d" sublevel is filled successively.
- It lies in the fourth period and includes the elements from scandium (21Sc) to zinc (30Zn).

② The second transition series:

- It includes the elements in which the "4d" sublevel is filled successively.
- It lies in the fifth period and includes the elements from yttrium (39Y) to cadmium (48Cd).

1 The third transition series:

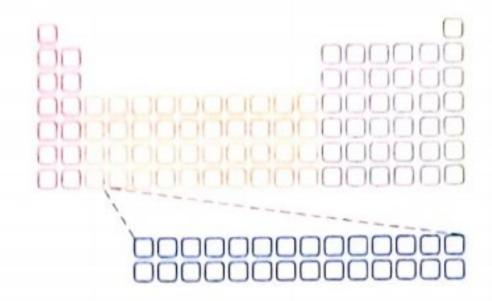
- It includes the elements in which the "5d" sublevel is filled successively.
- It lies in the sixth period and includes the elements from lanthanum (57La) to mercury (80Hg), "excluding lanthanides".

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f-block elements

- They are separated down the table, to avoid being a very wide table.
- In which the "f" sublevel is filled successively.
- The f-block is divided into two series each of them includes "14" elements which are.



Lanthanides series	Ce 4f'	Pr 4f ²	Nd 4f	Pm 4f '	Sm 4f	Eu 4f 7	Gd 4f	Tb 4f 8	Dy 4f "	Ho 4f 10	Er 4f ¹¹	Tm 4f 12	Yb 4f 14	Lu 4f14
Lanthanides series Actinides series	Th 5f	Pa 5f 2	U 5f 3	Np 5f	Pu 5f 5	Am 5f 7	Cm 5f 7	Bk 5f 8	Cf 5f°	Es 5f 10	Fm 5f 11	Md 5f 12	No 5f 14	Lr 5f14

f-block

1 The lanthanides series:

- It is placed in sixth period, in which the "4f" sublevel is filled successively.
- The elements of this series were named wrong by rare Earth's elements. GR.

 Because they are quite similar in behavior and very difficult to be separated as the outermost energy level for all of them is 6s²

 However, that name isn't accurrate, as recently their oxides can be separated by ionic exchange.

The actinides series :

- It is placed in seventh period, in which the "5f" sublevel is filled successively.
- All the elements of this series are radioactive and their nuclei are unstable.

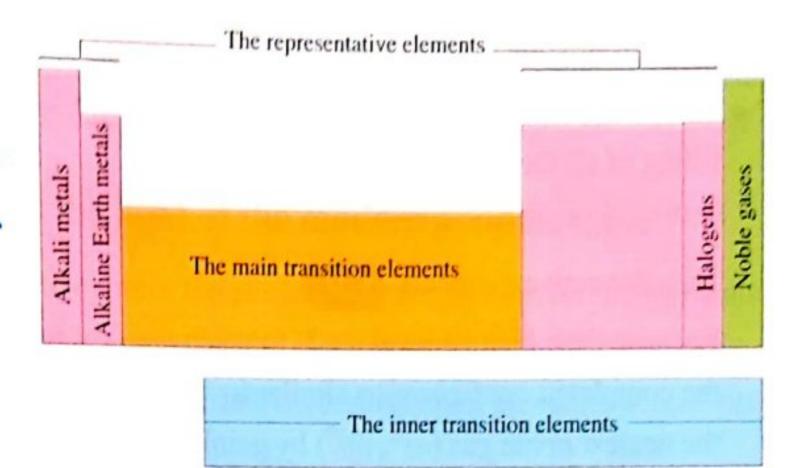
Give reason :

The number of elements of any series of the f-block is 14 elements, while d-block contains 10 elements.

Because f-block elements in which the f-sublevel is successively filled and it consists of 7 orbitals, while d-block elements in which the d-sublevel consists of 5 orbitals and each orbital is occupied by 2 electrons.

The type of the periodic table elements

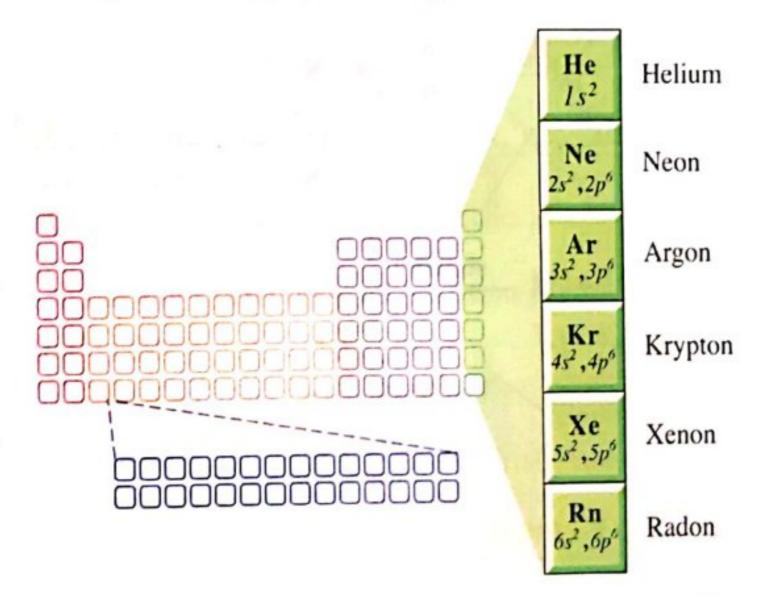
- It is possible to classify the elements in periodic table into four types, which are :
- O Noble gases.
- The representative elements.
- 10 The main transition elements.
- The inner transition elements.



The types of the periodic table elements

Noble gases

- They are the elements of the zero group "18" which is the last column of the p-block.
- They are characterized by having energy levels completely filled by electrons and their electronic structure is np^6 , except that of helium 2He which is $1s^2$



Noble gases

Give reason :

Noble gases may form compounds, but with great difficulty.

Because they are very stable elements as their energy levels are completely filled by electrons.



The representative elements

- They are the elements of s and p-blocks, except that of zero group.
- They occupy the groups from 1A: 7A
- These elements are characterized by the complete filling of all the energy levels with electrons, except for the highest level.
- They are active elements. GR. Because their highest level tends to reach the completed configuration similar to the nearest noble gas (ns^2, np^6) by gaining, losing or sharing electrons.

						1
		7A	0	1A	2A	34
5A	6A		He	Li ⁺	Be2*	
N3-	02-	F	Ne Ne	Na ⁺	Mg ²⁺	Al
	S ²⁻	CI	Ar	K ⁺	Ca ² +	
		Br	¾ Kr	Rb ⁺	Sr ²⁺	
		Г	54 Xe	Cs ⁺	Ba ²⁺	

The representative elements tend to reach the electron configuration of the nearest noble gas.

Examples

11Na
$$\frac{loses}{1 \text{ electron}}$$
 Na⁺

1s², 2s², 2p⁶, 3s¹

1s², 2s², 2p⁶

(Similar to the electronic configuration of neon gas 10Ne)

16S
$$\frac{\text{gains}}{2 \text{ electrons}}$$
 S⁻⁻

1s², 2s², 2p⁶, 3s², 3p⁴

1s², 2s², 2p⁶, 3s², 3p⁶

(Similar to the electronic configuration of argon gas $_{18}\text{Ar}$)

$$_{1}H + _{1}H \xrightarrow{\text{sharing}} H_{2}$$
 $_{1s^{l}} Is^{l}$
 $_{1s^{2}}$

(Similar to the electronic configuration of helium gas ₂He)

The main transition elements

- They are the elements of the d-block.
- They are characterized by having energy levels completely filled by electrons, except the two outermost levels.

Example
$$_{21}Sc:1s^2$$
,

21Sc:
$$1s^2$$
, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^2$, $3d^1$



- They are the elements of the f-block.
- They are characterized by having energy levels completely filled with electrons, except the three outermost levels.

Example $_{64}Gd: 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^7, 5d^1$

The electronic configuration in the light of the modern periodic table

• The periodic table shows a method to express the electronic configuration for the elements according to the nearest noble gas which precedes the element in the periodic table and this is considered the fourth method to the electronic configuration of elements which was mentioned before in the chapter one.

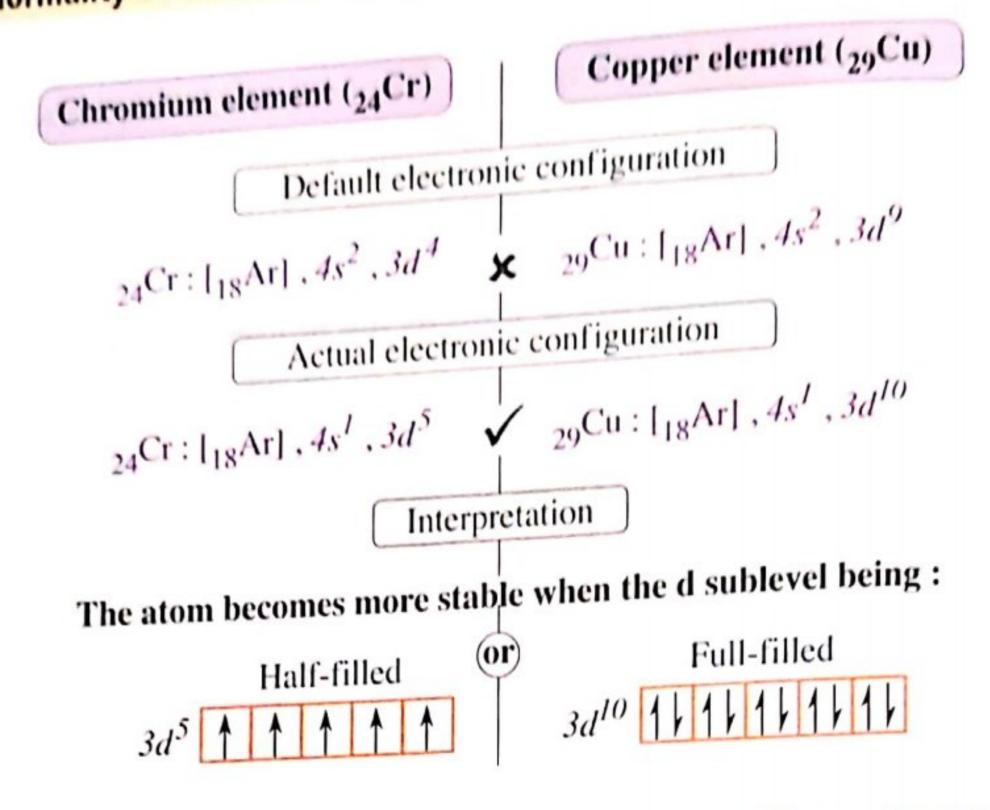
He 25 2p'Ne 18 35 3p'CI Ar 36 **Kr** 4p'5p'Cd Xe 56 Ba 5d6p'Rn 7p

• The following table shows the electronic configuration of illustrated elements in the previous periodic table :

The ordinary electronic configuration	Electronic configuration of the nearest noble gas principle
$17^{\text{Cl}}: 1s^2, 2s^2, 2p^6, 3s^2, 3p^5$	$_{17}\text{Cl}:[_{10}\text{Ne}], 3s^2, 3p^5$
26Fe : $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^2$, $3d^6$	$_{26}$ Fe: [$_{18}$ Ar], $4s^2$, $3d^6$
48Cd : $[1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}]$	$_{48}\text{Cd}:[_{36}\text{Kr}], 5s^2, 4d^{10}$
56Ba : $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^2$, $3d^{10}$, $4p^6$, $5s^2$, $4d^{10}$, $5p^6$, $6s^2$	56Ba: [54Xe], 6s ²



The abnormality of electronic configuration for some elements of the periodic table



9 By the same way the electronic configuration for Molybdenum (42Mo) and Gadolinium (64Gd)

Determination of the element location in the periodic table

- Period number: It is determined by the greatest principal quantum number (n) in the electronic configuration of the element.
- Group number and symbol :

They are determined by the type of element as shown in the following table:

Type of element	Group number	Group symbol	
	S	The number of electrons of the last sublevel (s).	
Representative	The sum of the numbers of electrons in the last two sublevels (s) and (p) .	A	
Noble gases	p	Zero group (the <i>p</i> -sublevel is completely filled by electrons).	-
Main transition	d	The sum of the numbers of electrons in the last (s) sublevel and the penultimate (d) sublevel.	В

• If the sublevel (n-1)d contains 6, 7, 8 electrons, the element is located in the group 8.

• If the electronic configuration of the element ends with:

$$\frac{1}{n}$$
, $\frac{1}{n}$, $\frac{(n-1)d^{10}}{n}$: the element is located in 1B group.

$$ns^2$$
, $(n-1)d^{10}$: the element is located in 2B group.

Examples

(1) Illustrate the block, type and location for the following elements in the periodic table : ${}_{12}Mg \ , {}_{32}Ge \ , {}_{36}Kr \ , {}_{25}Mn \ , {}_{29}Cu$

Solution

Element	Electronic configuration	Block	Type of element	Period number	Group number
12 ^{Mg}	$[_{10}Ne], 3s^2$	S	Representative	3	2A
32Ge	$[_{18}\text{Ar}]$, $4s^2$, $3d^{10}$, $4p^2$	p	Representative	4	4A
36Kr	$[_{18}\text{Ar}]$, $4s^2$, $3d^{10}$, $4p^6$	р	Noble gas	4	(18) zero
₂₅ Mn	$[_{18}Ar]$, $4s^2$, $3d^5$	d	Main transition	4	7B
₂₉ Cu	$[_{18}Ar]$, $4s^{I}$, $3d^{IO}$	d	Main transition	4	1B

- (2) A representative element contains four principal energy levels, the last level has three unpaired electrons, determine each of the following:
 - (a) Its electronic configuration.
 - (b) Its atomic number.
 - (c) Number of full-filled orbitals in the outermost energy level.
 - (d) Number of valence electrons.

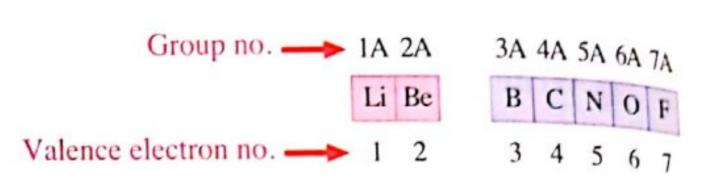
Solution

- (a) $[_{18}Ar]$, $4s^2$, $3d^{10}$, $4p^3$
- (b) 33
- (c) 1 orbital.
- (d) 5 electrons.



The graduation of the representative elements properties

The chemical properties and some of the physical properties of the elements depend on their electronic structure and especially on the valence electrons (the electrons of the outermost level).



The valence electron numbers for the elements of the second period

We will study the graduation of the following properties for the representative elements:

- 1 The radius property.
- Electron affinity.
- (a) Metallic and nonmetallic property.
- Oxidation numbers.

- ② Ionization potential.
- Electronegativity.
- (1) Acidic and basic property.



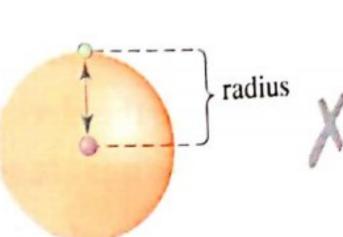
1 The radius property

- The concept of bond length differs in the covalent compounds from that in the ionic compounds.
- Through our knowledge by the bond length, we can calculate:
 - (A) Atomic radius.
- (B) Ionic radius.

A Atomic radius

• The atomic radius can't be calculated from the distance between the nucleus and the farthest electron. GR.

Because it is impossible to determine the precise location of an electron around the nucleus (as the wave mechanics revealed).



Wrong perception for the radius

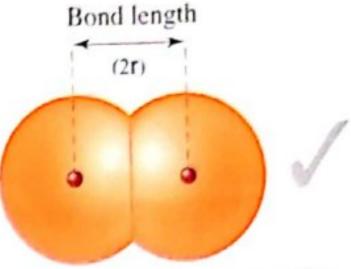
But the atomic radius can be calculated by knowing the covalent bond length which got measured by Angestrom unit (Å).

Covalent bond length (2r)

It is the distance between the nuclei of two bonded atoms.

Atomic radius (r)

It is half the distance between the centers of two similar atoms in a diatomic molecule.



Covalent Bond length (2r)

Covalent bond length = sum of the two atomic radii of the molecule

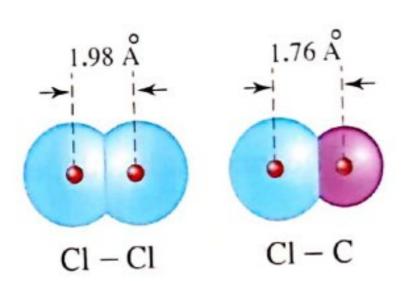
bond length in a diatomic element molecule (2r) The atomic radius (r) =

The following table shows the bond length and covalent atomic radius for some molecules:

The molecule	H-H	F-F	CI – CI	Br – Br	I – I
The bond length by A	0.60	1.28	1.98	2.28	2.66
The covalent atomic radius	0.30	0.64	0.99	1.14	1.33

Examples

1 The bond length in chlorine molecule Cl - Cl is 1.98 Å and the bond length between carbon and chlorine atoms C - Cl in carbon tetrachloride CCl₄ is 1.76 Å. Calculate the atomic radius of carbon.



Solution

The atomic radius of chlorine =
$$\frac{\text{bond length}}{2} = \frac{1.98}{2} = 0.99 \text{ Å}$$

The atomic radius of carbon = the bond length between carbon and chlorine - the atomic radius of chlorine

$$= 1.76 - 0.99 = 0.77 \,\text{Å}$$

1 The bond length in hydrogen molecule H-H is $0.6\,\text{Å}$, the bond length of nitrogen molecule N_2 is 1.4 Å and the bond length of nitric oxide molecule NO is 1.36 Å.

Calculate:

- The bond length in oxygen molecule.
- **1** The bond length (O H) in water molecule H_2O



Solution

The atomic radius of nitrogen = $\frac{\text{bond length}}{2} = \frac{1.4}{2} = 0.7 \text{ Å}$ The atomic radius of oxygen = the bond length of nitric oxide molecule – the atomic radius of nitrogen

$$= 1.36 - 0.7 = 0.66 \text{ Å}$$

The bond length in oxygen molecule = $2 \times$ the atomic radius of oxygen = $2 \times 0.66 = 1.32 \text{ Å}$

The atomic radius of hydrogen =
$$\frac{\text{bond length}}{2} = \frac{0.6}{2} = 0.3 \text{ Å}$$

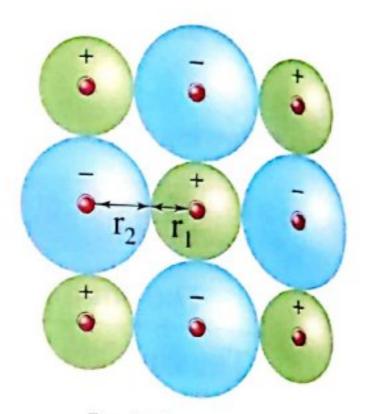
The bond length (O – H) = the atomic radius of oxygen + the atomic radius of hydrogen = $0.66 + 0.3 = 0.96 \text{ Å}$

B Ionic radius

The ionic compounds as sodium chloride are found in a crystalline form and consist of positive ions (cations) and negative ions (anions).

lonic bond length

It is the distance between the centers of the nuclei of two bonded ions.



Ionic bond length Radius of (cation + anion)

The ionic bond length = the sum of two ionic radii of the formula unit

• The ionic radius depends on the number of electrons lost or gained to form ions.

Example

- The ionic radius of lithium (Li⁺) = 0.68 Å
- The ionic radius of sodium (Na⁺) = 0.98 Å
- The bond length of sodium chloride formula unit (Na⁺Cl⁻) = 2.76 Å Calculate the ionic bond length in lithium chloride molecule.

Solution

• The ionic radius of Cl⁻ = the bond length of sodium chloride formula unit

– the ionic radius of sodium

$$= 2.76 - 0.98 = 1.78 \,\text{Å}$$

• The bond length in lithium chloride formula unit (Li⁺Cl⁻) = the ionic radius of Li⁺ + the ionic radius of Cl⁻ = 0.68 + 1.78 = 2.46 Å

The effective nuclear charge concept (Z_{eff})

The valence electrons are not affected by the complete nuclear charge (the charge of the nucleus protons).

This is because the inner electrons (of the inner energy levels) screen a part of this charge from the valence electrons. So, the actual charge affecting any electron is called the effective nuclear charge Z_{eff}

Nucleus Attraction Repulsion

The attraction and repulsive forces which affect the valence electrons

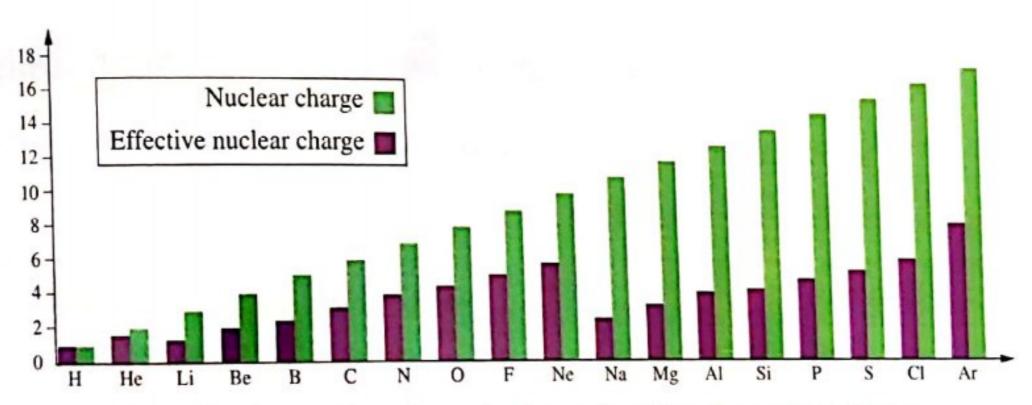
Effective nuclear charge (Zeff)

It is the actual nuclear charge (positive charge) which affects an electron in an atom.

Give reason :

The effective nuclear charge (Z_{eff}) is always less than the nuclear charge (the total number of protons present in a nucleus).

Due to the screening effect of the electrons of the inner energy levels on a part of the nuclear charge affecting the electrons under study.



The effective nuclear charge is always less than the nuclear charge

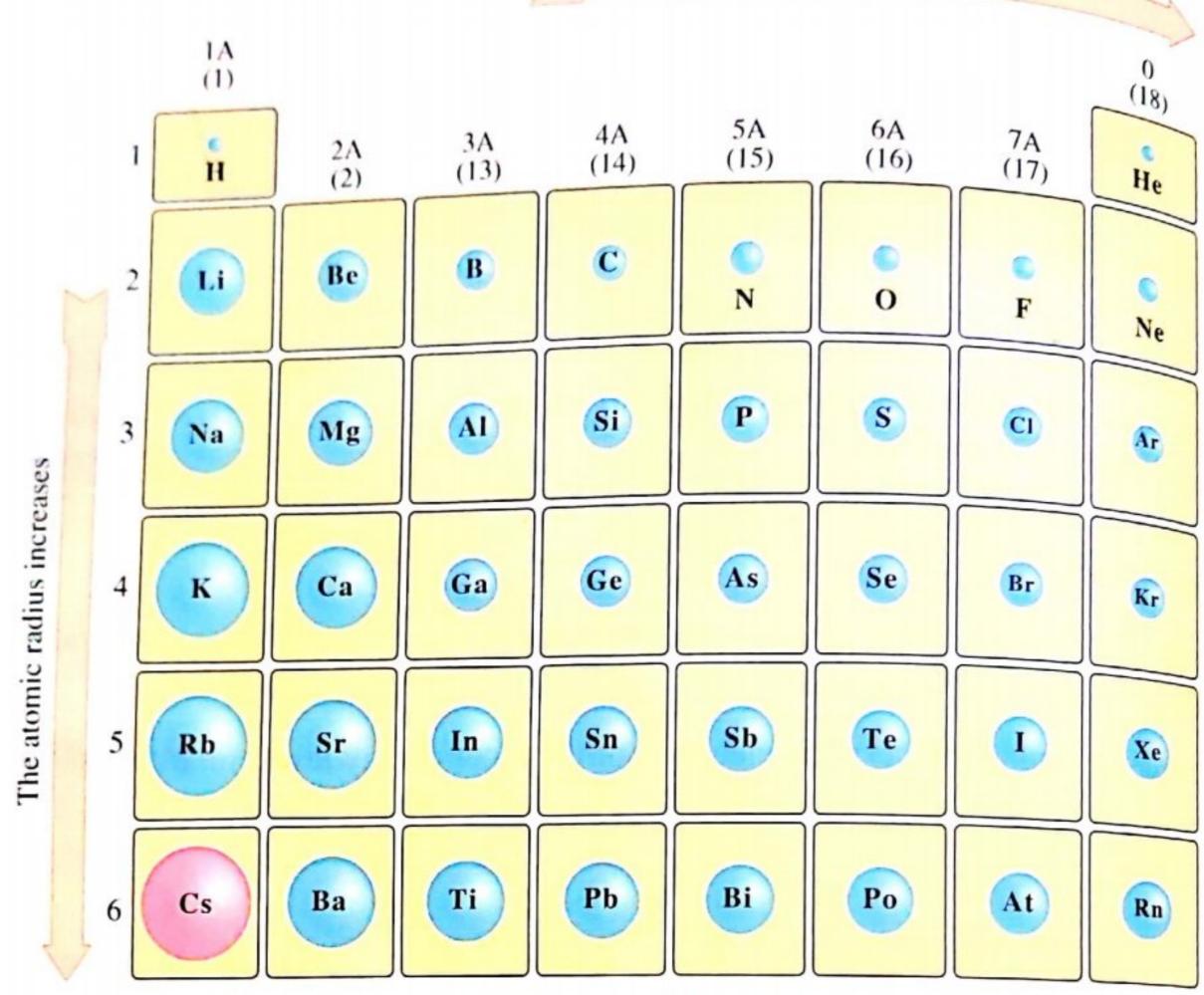
The element	Li	Be	B	C	N	0	F	Ne
Z	3	4	5	6	7	8	9	10
Z _{eff}	1.28	1.91	2.42	3.14	3.83	4.45	5.10	5.76

For illustration only



The graduation of atomic radius property in the periodic table

The atomic radius decreases



The graduation of atomic radius in the representative elements

t It can be observed from the figure that :

In the horizontal period	In the vertical group
The atomic radius decreases as we go from the left to right across a period by increasing the atomic number from 1A to zero group.	The atomic radius increases as we go down the group by increasing the atomic number from the first period to seventh.
This is	due to
The gradual increase in the effective nuclear charge ($Z_{\rm eff}$) which increases the nuclear attraction force on the valence electrons leading to the reduction of the atomic radius.	 The increase in the number of the energy levels in each new period. The increase in the number of the filled energy levels that having a screening effect on the pull of the nuclear charge on the outer electrons. The increasing of the repulsive forces between electrons.

Subsequently that: The atoms of the seventh group elements (halogens) are the biggest atoms, while

The atoms of the seventh group elements (halogens) are the biggest atoms, while the atoms of the seventh group elements (halogens) are the smallest atoms. The biggest atom in size is cesium (Cs).

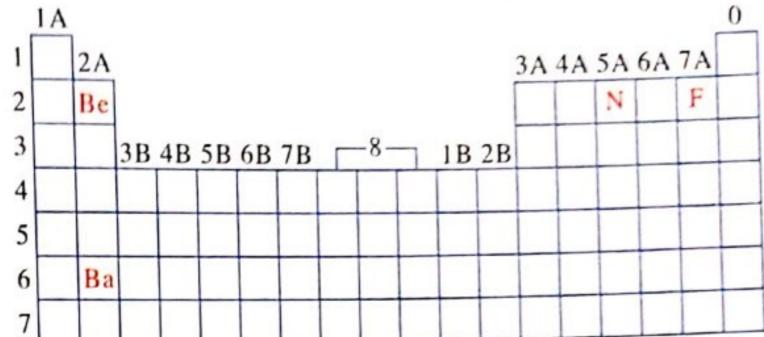
In the light of your knowledge about the graduation of the atomic radius property in

the periodic table.

Mention which atom is larger in size in each of the following pairs of atoms with an explanation for your answer:

0 7N.9F

20 56Ba, 4Be



Solution

(N) atom is bigger than (F) atom. Because the atomic size decreases in the same period as we go from left to right by increasing the atomic number.

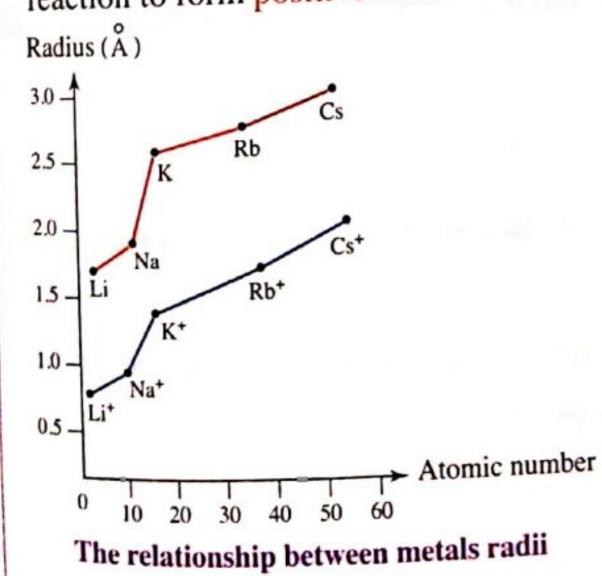
(Ba) atom is bigger than (Be) atom. Because the atomic size increases in the same group as we go down the group by increasing the atomic number.

The relation between the radii of atoms and their ions

• The radii of atoms differ from the radii of their ions as shown in the following:

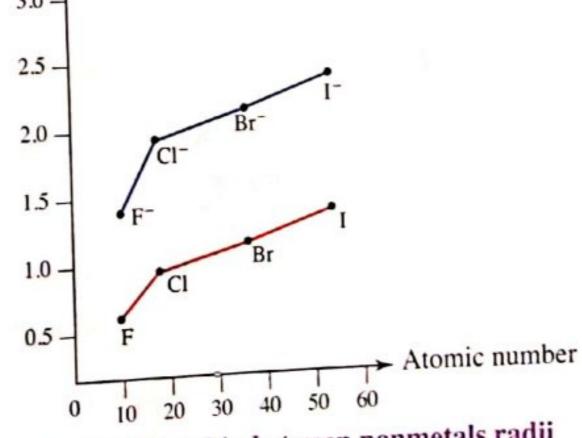
Metals

• The metal atoms tend to lose their valence electrons during the chemical reaction to form positive ions.



and their positive ions.

- **Nonmetals**
- The nonmetal atoms tend to gain electrons during the chemical reaction to form negative ions. Radius (A) 3.0 -2.5



The relationship between nonmetals radii and their negative ions.



The positive ion radius is smaller than its atomic radius.

• The number of positive protons in the cation (positive ion) is larger than the number of negative electrons. So, the attraction force of the effective nuclear charge on remaining electrons increases leading to decrease the size.

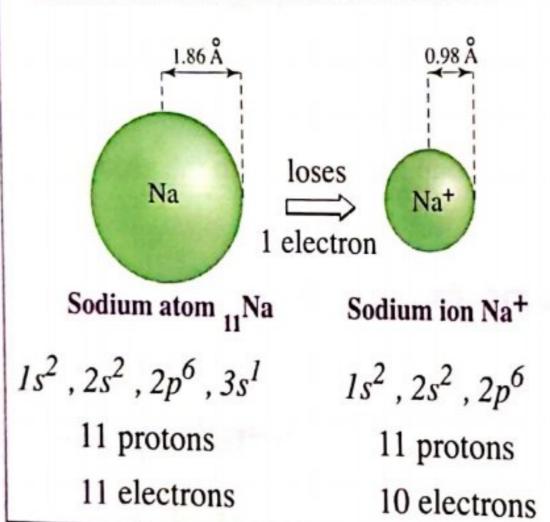
The negative ion radius is larger than its atomic radius.

Because

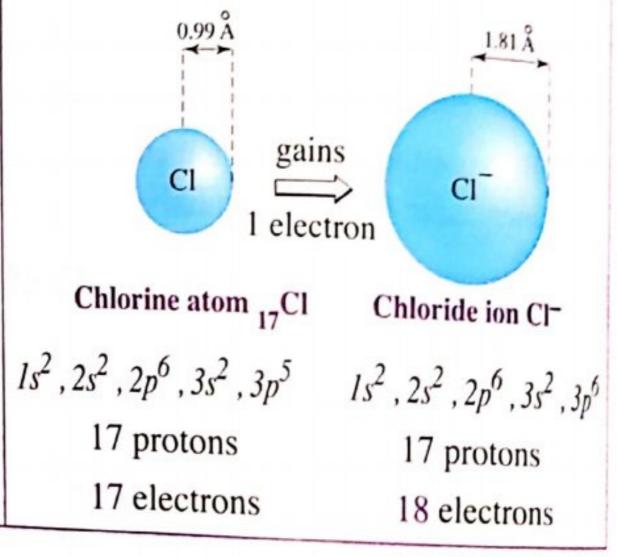
the number of negative electrons in the anion (negative ion) is larger than the number of positive protons. So, the **repulsive forces** between electrons increase due to increasing the number of electrons without any increasing in the nuclear charge leading to increase the size.

Application

 The sodium metal tends to lose its valence electron during chemical reactions to form sodium ion of radius smaller than the radius of its atom.



• The chlorine nonmetal tends to gain an electron during chemical reactions to form chloride ion of radius larger than the radius of its atom.



• The ionic radius decreases as the effective nuclear (positive) charge of the ion increases.

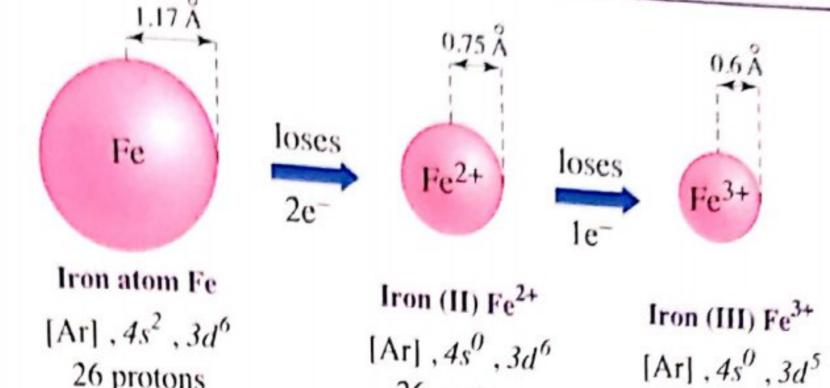


Application

The atomic radius of iron atom (Fe) > the ionic radius of iron (II) ion Fe^{2+} > the ionic radius of iron (III) ion Fe^{3+}

Because the atomic radii of metals are bigger than the radii of their ions. As the ionic radius of positive ion decreases, when its charge increases.

26 protons



24 electrons 23 electrons Ionic radius of positive ion decreases as its charge increases

26 protons

Jonization potential (Ionization energy)

26 protons

26 electrons

If an energy is supplied to an atom, electrons may be excited and transferred to higher energy levels, but if a sufficient energy is supplied, the most loosely bound electron may be completely removed, giving a positive ion. The minimum amount of this energy is called ionization potential

Ionization potential (Ionization energy)

It is the amount of energy required to remove the most loosely bound electron completely from an isolated gaseous atom.

• ΔH of the ionization process has a positive sign. GR. Because the ionization energy is an absorbed energy.

Na_(g) + Energy
$$\longrightarrow$$
 Na_(g) + e⁻ , $\Delta H = +496 \text{ kJ/mol}$
[₁₀Ne], $3s^I$ [₁₀Ne], $3s^0$

• The atom of the same element has more than ionization energy as shown in the following:

First ionization potential	Second ionization potential	Third ionization potential			
It is the amount of energy required to convert an isolated gaseous atom to an ion carries one positive charge.	It is the amount of energy required to remove an electron from a positive ion carries one positive charge.	It is the amount of energy required to remove an electron from a positive ion carries two positive charges.			
$M_{(g)}$ + Energy \longrightarrow	$M_{(g)}^+$ + Energy \longrightarrow	$M_{(g)}^{2+}$ + Energy \longrightarrow			
$M_{(g)}^+ + e^-, \Delta H = (+)$	$M_{(g)}^{2+} + e^-, \Delta H = (+)$	$M_{(g)}^{2+}$ + Energy \longrightarrow $M_{(g)}^{3+}$ + e^- , $\Delta H = (+)$			
The first ionization notential	the second ionization potential	< the third ionization potential.			



Application

The first ionization potential of noble gases and alkali metals.



Ionization potential (kJ/mol) 2000 1500 Mg 1000 500 Atomic number 15 10 5

• The first ionization potential of noble gases is very high. GR. Due to the stability of their electronic configuration and it is difficult to remove an electron from a completely filled shell.

Examples

 $_{10}$ Ne: [$_{2}$ He], $2s^{2}$, $2p^{6}$ $_{18}$ Ar: [$_{10}$ Ne], $3s^{2}$, $3p^{6}$

• The first ionization energy of alkali metals is lower than that of all elements. CR Due to the easily loss of the valence electron.

Examples

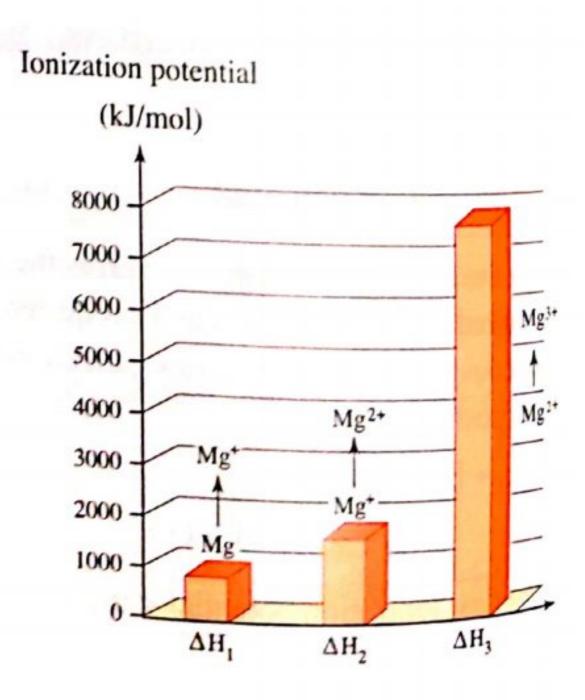
 $_{11}$ Na: [$_{10}$ Ne], $_{3s}^{I}$ $_{19}$ K: [$_{18}$ Ar], $_{4s}^{I}$

Application

The ionization potentials of magnesium:

The corresponding figure expresses the ionization potentials of magnesium and it's clear that:

- The second ionization energy of magnesium is greater than the first one. GR. Due to the increasing of the effective nuclear charge (Z_{eff}).
- The third ionization potential of magnesium is much greater than that of its first and second ones. GR. Because it results in the breaking up of a completely filled energy level.

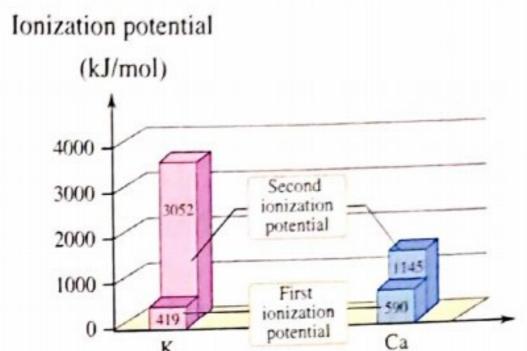


$$Mg_{(g)} \longrightarrow Mg_{(g)}^{+} + e^{-}, \Delta H_{1} = +737 \text{ kJ/mol}$$
 $Is^{2} \cdot 2s^{2} \cdot 2p^{6} \cdot 3s^{2}$
 $Is^{2} \cdot 2s^{2} \cdot 2p^{6} \cdot 3s^{1}$
 $Mg_{(g)}^{+} \longrightarrow Mg_{(g)}^{2+} + e^{-}, \Delta H_{2} = +1450 \text{ kJ/mol}$
 $Is^{2} \cdot 2s^{2} \cdot 2p^{6} \cdot 3s^{1}$
 $Is^{2} \cdot 2s^{2} \cdot 2p^{6}$
 $Mg_{(g)}^{2+} \longrightarrow Mg_{(g)}^{3+} + e^{-}, \Delta H_{3} = +7730 \text{ kJ/mol}$
 $Is^{2} \cdot 2s^{2} \cdot 2p^{6}$
 $Is^{2} \cdot 2s^{2} \cdot 2p^{5}$

@ Give reason:

The first ionization potential of potassium 19K is lower than that of calcium 20Ca, while the second ionization potential of potassium is much greater than that of calcium.

$$_{19}$$
K:[$_{18}$ Ar], $_{4s}^{I}$, $_{20}$ Ca:[$_{18}$ Ar], $_{4s}^{2}$



Ionization potentials of potassium and calcium

The first ionization potential of potassium is lower than that of calcium due to the easily loss of the valence electron, while the second ionization potential of potassium is much greater than that of calcium because it results in the breaking up of a completely filled shell.

The graduation of ionization potential in the periodic table :

In the same period	In the same group
The first ionization potential increases as we move from left to right.	The first ionization energy decreases as we go down the group.
Ionization potential (kJ /mol) 2500 1500 1500 100	The state of the s
Pernod Cie as Cie as S	nization potential property



This is due to

The increase of the effective nuclear charge and the decrease of the atomic radius, which would lead to increase the attraction force of the nucleus on the valence electrons, which need higher energy to separate them from the atom.

- The extra shells of electrons are added which increase the atomic radius.
- The decrease of attraction force of the nucleus on the valence electrons. So, the energy required to remove the valence electrons decreases.

So, the ionization potential is inversely proportional to the atomic radius.

Give reasons:

The ionization potential of oxygen 80 is lower than that of nitrogen 7N, although oxygen

Because the atom becomes more stable when the 2p sublevel is half-filled by electrons as in nitrogen atom and removing an electron from it will decrease its stability.

The ionization potential of aluminum 13Al is lower than that of magnesium 12Mg, although aluminum comes next magnesium in the same period.

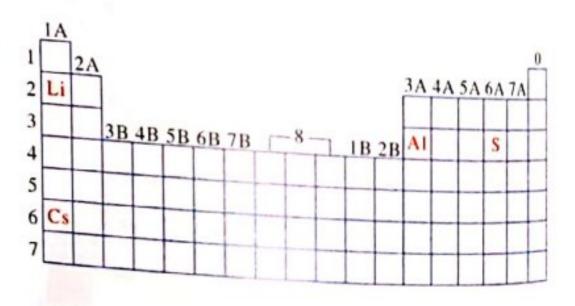
$$_{12}$$
Mg: [$_{10}$ Ne], 3s² $_{13}$ Al: [$_{10}$ Ne], 3s², 3p¹

Because the atom becomes more stable when the 3s-sublevel is full-filled by electrons as in magnesium atom and removing an electron from it will decrease its stability.

Example

In the light of your knowledge for the graduation of ionization potential in the periodic table:

Mention which atom is higher in ionization potential in each of the following pairs of atoms with an explanation for your answer.



Solution

- The ionization potential of 16S is greater than that of 13Al, because the ionization potential increases in the same period as we move from left to right by increasing the atomic number.
- The ionization potential of 3Li is greater than that of 55Cs, because the ionization potential decreases in the same group as we go down the group by increasing the atomic number.

3 Electron affinity

We have mentioned that the removal of an electron from the atom will convert it into a cation, which requires an amount of energy named by the first ionization energy. On the other hand, if the atom gained an extra electron, it will be converted into a negative ion. This is associated with releasing an amount of energy named by electron affinity.

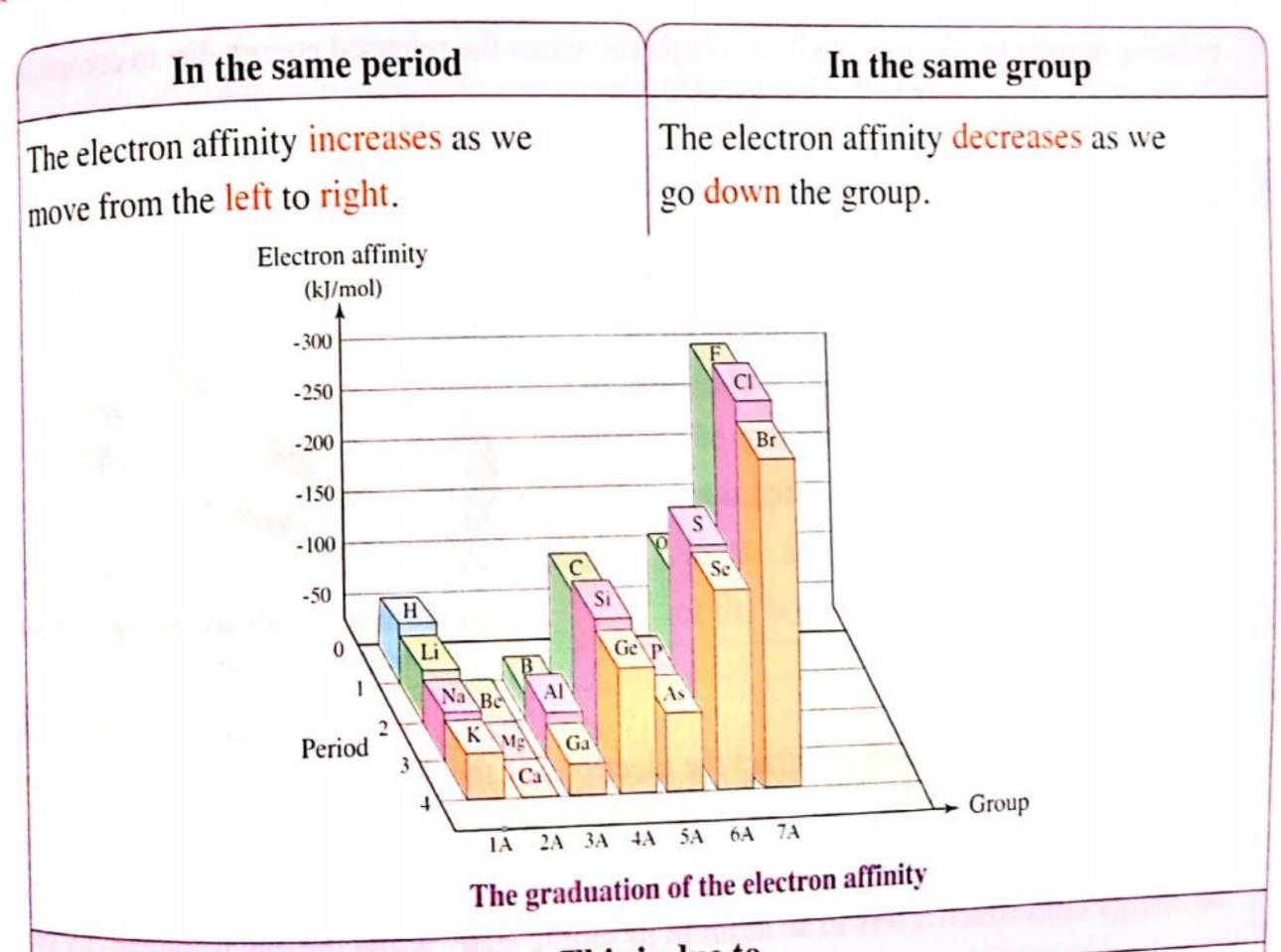
Electron affinity

It is the amount of energy released when an extra electron is added to a neutral gaseous atom.

$$X_{(g)} + e^- \longrightarrow X_{(g)}^- + Energy, \Delta H = (-)$$

The magnitude of the electron affinity is high when the added electron makes the sublevel, half-filled or completely filled, as in both cases it helps in the stability of the atom.

The graduation of electron affinity in the periodic table :



This is due to

The increase of the atomic number leading to the decrease of atomic radius (atomic size), which makes it easier for the nucleus to attract a new electron.

The increase of the atomic number leading to the increase of atomic radius (atomic size). So, the ability of the nucleus to attract the new electron decreases.



Give reasons:

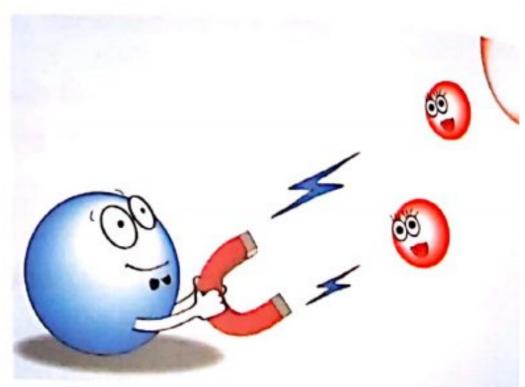
The electron affinity values for beryllium, nitrogen and neon are close to zero, $_4\text{Be}: 1s^2, 2s^2$, $_7\text{N}: 1s^2, 2s^2, 2p^3$, $_{10}\text{Ne}: 1s^2, 2s^2, 2p^6$

Because the atom will be more stable when the sublevel:

- 2s is full-filled as in case of beryllium atom 4Be
- 2p is half-filled as in case of nitrogen atom 7N
- 2p is full-filled as in case of neon atom 10^{Ne} and the addition of an electron to any atom of them will decrease its stability.
- The electron affinity of chlorine (- 348.6 kJ/mol) is greater than the electron affinity of fluorine (- 328 kJ/mol), although chlorine comes next fluorine through the same group. Because fluorine atom is smaller in size as it has smaller radius than chlorine atom. So, the entering of an electron will suffer a strong repulsive force with the nine electrons already existing around the fluorine nucleus which decreases the released energy due to consuming a part of it to overcome this repulsive force.

4 Electronegativity

• When two atoms of two different elements combine together, the ability of one atom of them to attract the electrons of the chemical bond towards itself differs from that of the other atom, this attraction force is named by electronegativity.



The electronegativity for the elements of the representative groups

Electronegativity

It is the tendency of an atom to attract the electrons of the chemical bond to itself.

- The electron affinity differs from the electronegativity, where the electron affinity is an energy term which refers to an atom in its single state, while the electronegativity of the elements is represented by relative values and it refers to a combined atom.
 - * The increase of the relative values of the electronegativity means the increase in the ability of the element atom to attract the electrons of the chemical bond.



* The difference in electronegativity between elements plays a very important role in chapter three).

The graduation of electronegativity in the periodic table :

In the same period In the same group The electronegativity increases as we The electronegativity decreases as we move from left to right. go down the group. Electronegativity 3.0:4.0 2.0:2.8 1.5:1.9 < 1.5 period The graduation of the electronegativity This is due to The increase of the atomic number The increase of the atomic number leading leading to the increase of atomic radius. to the decrease of atomic radius. So, So, the ability of atom to attract electrons

Subsequently that:

the ability of atom to attract the electrons

of the bond towards itself increases.

• The atoms of nonmetals group 7A (halogens) are the greatest in the electronegativity, while the atoms of the alkali metals group 1A are the lowest in the electronegativity.

of the bond towards itself decreases.

• Fluorine (F) is considered to be the most electronegative element, while cesium (Cs) is considered to be the lowest electronegative element.



From: Metallic and nonmetallic property

: The oxidation numbers To

Metallic and nonmetallic property

At the beginning of the nineteenth century "Berzelius" was the first scientist who classified elements into two main groups (metals and nonmetals), according to their physical properties. Indeed that was before knowing anything about atomic structure.

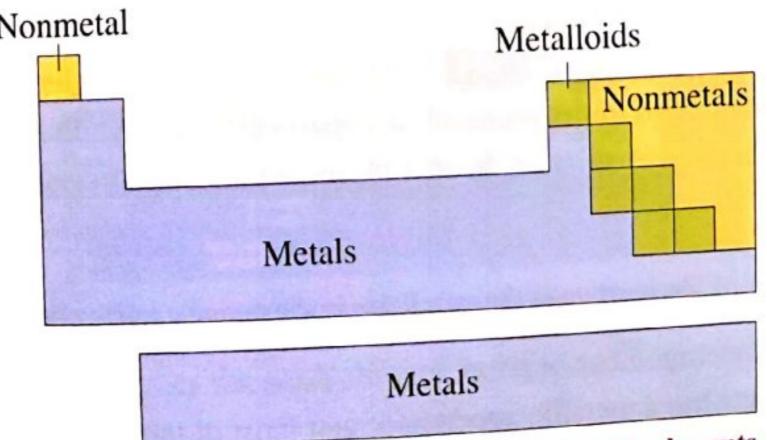


• This is an old classification which is still currently in use, although there are no boundaries between them and their properties in the periodic table.



With the development of our concept about the electronic structure of atoms, we can differentiate between metals and nonmetals. Additionally, there is a third group of elements known as metalloids.

Metalloids. Nonmetals. 0 Metals. Nonmetal Metalloids



Classification of the modern periodic table elements into metals, nonmetals and metalloids



Metals

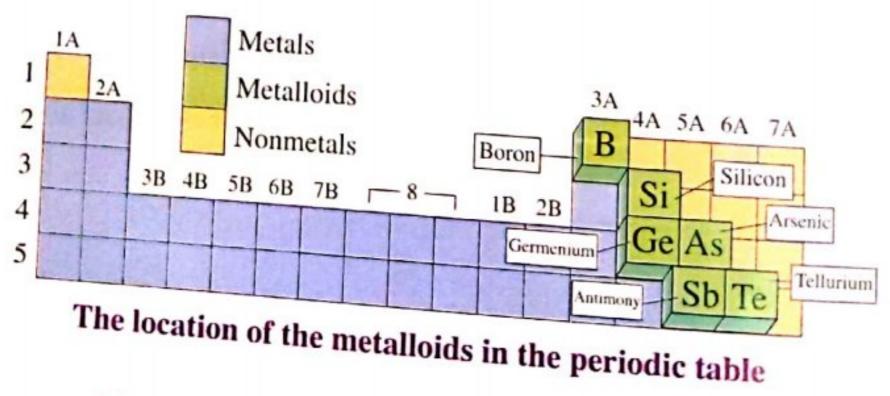
- Their valence shell generally has less than half its capacity of electrons.
- They have large atomic radius which leads to small values for ionization energy and electron affinity.
- They are electropositive elements. GR. Due to their tendency to lose electrons of the valence shell and change into positive ions to reach the structure of the nearest noble gas.
- They are good electric conductors. GR. Due to the mobility of their few valence electrons, which can transfer from one position to another in the metal structure.

Nonmetals

- Their valence shell generally has more than half its capacity of electrons.
- 2 They have small atomic radius which leads to high values for ionization energy and electron affinity.
- They are electronegative elements. GR Due to their tendency to gain electrons to form negative ions that have the same electron structure of the nearest noble gas.
- They don't conduct electricity (electric insulators). GR. Because their valence electrons are strongly bound to the nucleus. Thus, it is difficult for these valence electrons to be transferred.

Metalloids:

- The metalloids are characterized by the following properties :
 - They have the metallic appearance and the most properties of nonmetals.
 - Their electronegativity is intermediate between metals and nonmetals.
- Their electric conductivity is less than that of metals, but more than that of nonmetals.
- They are used in manufacturing electronic instruments parts such as transistors as



Metalloids

A group of elements has a metallic appearance and most of the properties of nonmetals which characterized by their electronegativity is intermediate between metals and nonmetals and their electric conductivity is less than that of metals, but more than that of nonmetals.

The graduation of metallic and nonmetallic property in the periodic table :

	,	1A							
	1	Н	2A		3A	4A	5A	6A	7A
Metals	2	Li	Be		В	C	N	0	F
	3	Na	Mg		Al	Si	P	S	Cl
Metalloids	4	K	Ca	7	Ga	Ge	As	Se	Br
Nonmetals	5	Rb	Sr	35	In	Sn	Sb	Те	I
	6	Cs	Ba	3	Tl	Pb	Bi	Po	At

The graduation of metallic and nonmetallic property in the periodic table

In the same group:

• The metallic character increases (The nonmetallic character decreases) with the increase in the atomic number as we go down the group. GR. Due to their large atomic radius and the low ionization potential and electron affinity.

In the same period:

• The period begins by the strongest metals in group I A, then the metallic property decreases gradually by increasing the atomic number across the period till we reach the metalloids. To the right of the metalloids begins the nonmetallic property.

The period ends by the elements of the highest nonmetallic property in group 7A

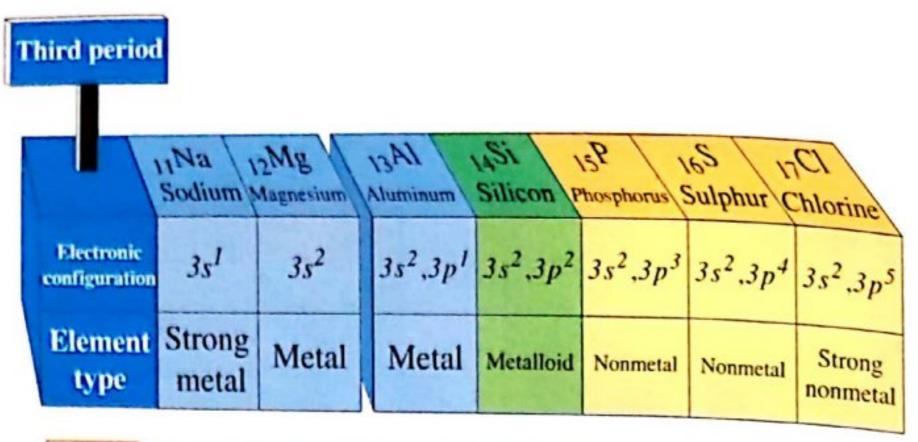
Consequently:

- Cesium is considered the most active metal. GR. Because the metallic property increases at the same group by increasing the atomic number and it is placed at the bottom of the left hand side of the table (the lowest metal in ionization potential).
- Fluorine is considered the most active nonmetal. GR Because the nonmetallic property decreases at the same group by increasing the atomic number and it is placed at the top of the right side of the table (the most electronegative nonmetal).

Application The graduation of metallic and nonmetallic property in the third period.

- The following figure expresses the graduation of metallic and nonmetallic property in the third period.
- It is clear that by increasing the atomic number, the metallic character decreases and the nonmetallic character increases.

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As the atomic number increases, the metallic property decreases and the nonmetallic property increases.

Acidic and basic property

- When an element combines with oxygen forming a compound known as oxide.
- There are three types of element oxides, which are :
 - Acidic oxides.
- Basic oxides.
- (B) Amphoteric oxides.

Acidic oxides

- The nonmetallic oxides are named by acidic oxides. GR. Because:
 - They dissolve in water forming oxygenated acids.

$$CO_{2(g)}$$
 + $H_2O_{(\ell)}$ \longrightarrow $H_2CO_{3(aq)}$ carbon dioxide water carbonic acid $SO_{3(g)}$ + $H_2O_{(\ell)}$ \longrightarrow $H_2SO_{4(aq)}$

$$SO_{3(g)}$$
 + $H_2O_{(l)}$ \longrightarrow $H_2SO_{4(aq)}$ sulphur trioxide water sulphuric acid

They react with alkalis forming salt and water.

$$CO_{2(g)}$$
 + $2NaOH_{(aq)}$ \longrightarrow $Na_2CO_{3(aq)}$ + $H_2O_{(l)}$ \longrightarrow $Basic oxides$ sodium hydroxide sodium carbonate water

Basic oxides

- The metallic oxides are usually known as basic oxides.
- Some basic oxides are not soluble in water and others are soluble in water forming alkalis, the water soluble basic oxides are also known as alkali oxides.

$$K_2O_{(s)}$$
 + $H_2O_{(l)}$ \longrightarrow 2KOH_(aq) potassium oxide water potassium hydroxide $Na_2O_{(s)}$ + $H_2O_{(l)}$ \longrightarrow 2NaOH_(aq) sodium oxide water sodium hydroxide

From the acidic oxides

- Carbon dioxide CO2
- Sulphur trioxide SO₃
- Nitrogen dioxide NO₂

From the basic oxides

- Potassium oxide K₂O
- Sodium oxide Na₂O
- Magnesium oxide MgO

Amphoteric oxides

Aluminum oxide Al₂O₃

Antimony oxide Sb₂O₃

Zinc oxide ZnO

Tin oxide SnO

$$Na_2O_{(s)}$$
 + $2HCl_{(aq)}$ \longrightarrow $2NaCl_{(aq)}$ + $H_2O_{(l)}$ sodium oxide hydrochloric acid sodium chloride water $MgO_{(s)}$ + $H_2SO_{4(aq)}$ \longrightarrow $MgSO_{4(aq)}$ + $H_2O_{(l)}$ magnesium oxide sulphuric acid magnesium sulphate water

C Amphoteric oxides

Amphoteric oxides

They are element oxides that react with acids as basic oxides and react with bases as acidic oxides forming in both cases salt and water.

$$ZnO_{(s)}$$
 + $H_2SO_{4(aq)}$ \longrightarrow $ZnSO_{4(aq)}$ + $H_2O_{(l)}$
zinc oxide sulphuric acid zinc sulphate water

 $ZnO_{(s)}$ + $2NaOH_{(aq)}$ \longrightarrow $Na_2ZnO_{2(aq)}$ + $H_2O_{(l)}$ zinc oxide sodium hydroxide (base) sodium zincate water

The graduation of acidic and basic property in the periodic table :

In the period	In the group				
The basic property of the oxide decreases as the atomic number of the element increases, while the acidic property increases.	In the group which starts by a metal	In the group which starts by a nonmetal			
	The basic property of the oxide increases as the atomic number increases as in group 1A	The acidic property of the oxide increases as the atomic number increases as in group 7A			

Application The graduation of acidic and basic property in the third period.

 The following figure expresses the graduation of acidic and basic property in the third period. It is shown that, as the atomic number increases the basic property decreases and the acidic property increases.

Third period		12Mg Magnesium	Aluminun	Silicon	12b	Sulphur	Chlorine
Element oxide	Na ₂ O	MgO	Al ₂ O	sio ₂	P ₂ O ₅	SO ₃	CI ₂ O ₇
Oxide type	Market Street	isic ide	Amphotes	0.00	Acidic	oxide	
The graduation	NaOH	Mg(OH) ₂	A1(OH	H ₄ SiO ₄	H ₃ PO ₄	H ₂ SO ₄	HCIO ₄
of the acidic and basic property	Strong base	Weak base	Amphoter	China Control of the	Moderate acid	Strong acid	Strongest acid

As the atomic number increases, the basic property decreases and the acidic property increases.



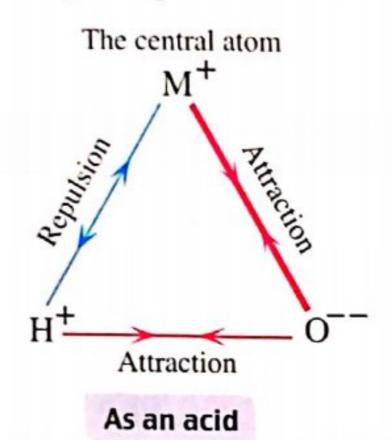
Give reason:

The acidic property of hydrogen compounds of group 17 (halogens) increases as the atomic number increases.

Because the increase in the atomic number in the group leads to the increase in the atomic size of halogen and then its attraction force for hydrogen atom decreases, making it easier to be ionized.

The acidic and basic property of the hydroxy compounds

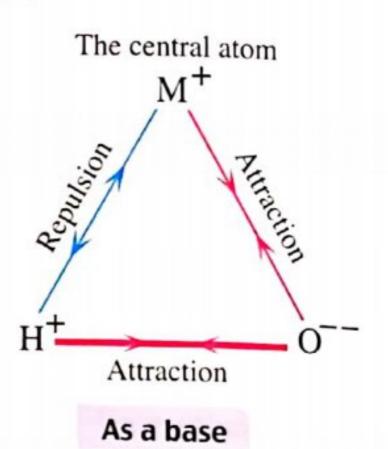
- The oxygenated acids (acids contain oxygen) and bases are considered as hydroxy compounds, they can be represented by the general formula (MOH), where M is the element atom.
- The hydroxy compounds can be ionized by either ways:



* The compound will be ionized as an acid if: The (M – O) bond is stronger than the (O – H) bond.

(i.e. The attraction force between M⁺ and O⁻⁻ is stronger than that between H⁺ and O⁻⁻).

$$MOH \longrightarrow MO^- + H^+$$
oxygenated acid hydrogen ion



Group (17

Fluorine

Chlorine

35Br

Bromine

Iodine

The graduation of

acidic property of

halogen

HF

HCl

HBr

HI

* The compound will be ionized as a base if: The (O – H) bond is stronger than the (M – O) bond.

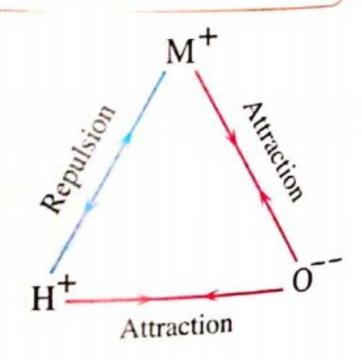
(i.e. The attraction force between H⁺ and O⁻⁻ is bigger than that between M⁺ and O⁻⁻).

$$\begin{array}{c} MOH \longrightarrow M^+ + OH^- \\ base & hydroxide ion \end{array}$$

Note

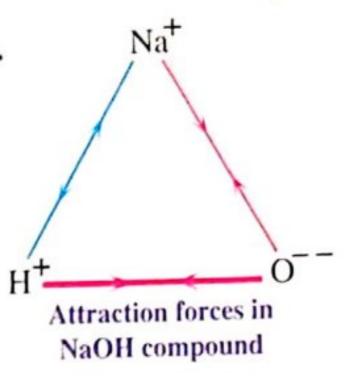
If the strength of (M - O) bond and the strength of (O - H) bond are equal, the substance will be ionized as an acid or a base depending on the reaction medium, this means that it reacts as a base in the acidic medium and as an acid in the basic medium.

- In general the attraction forces between each of (O^{--}, M^+) and (O^{--}, H^+) depend on :
 - The volume of atom M
 - The charge of M in the compound.



Application The basic property of sodium hydroxide compound.

Sodium hydroxide is ionized as a base, where sodium atom has a big volume and its ion has only one positive charge. Accordingly the attraction between Na⁺ and O⁻⁻ decreases i.e. The (O - H) bond is stronger than that of the (Na - O) bond. So, OH⁻ ion is produced.

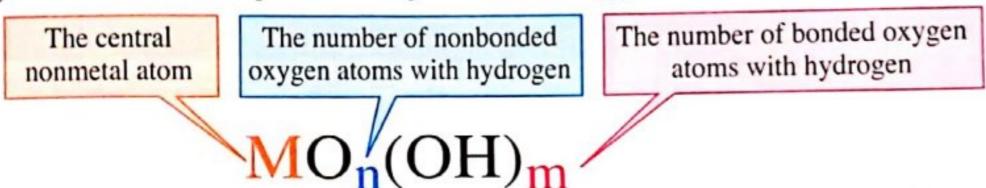


Give reason:

The hydroxy compounds of the nonmetallic elements as chlorine are ionized as an acid. Because the nonmetallic elements are characterized by the small atomic volume and the big charge which increase its attraction to O⁻⁻ ion and the (Cl - O) bond becomes stronger than the (O - H) bond. So, the positive hydrogen ion H⁺ is produced.

The strength of the oxygenated acids

• The oxygenated acids are represented by the following general formula:



 The strength of the oxygenated acid increases as the number of nonbonded oxygen atoms (On) with hydrogen increases as shown in the following table:

Acid	Orthosiliconic H ₄ SiO ₄	Orthophosphoric H ₃ PO ₄	Sulphuric H ₂ SO ₄	Perchloric HClO ₄
Hydroxyl	HO, OH HO' OH	O P HOOH OH	O O O O O O O O O O O O O O O O O O O	O O O O CI OH
formula MO _n (OH) _m				
	Si(OH) ₄	PO(OH) ₃	SO ₂ (OH) ₂	ClO ₃ (OH)
Ratio n : m	Zero	1:3	2:2	3:1
No. of nonbonded oxygen atoms with hydrogen	Zero	1	2	3
Strength of the acid	Weak	Moderate	Strong	The strongest



Summary of the elements graduation in the periodic table :

• Trends and periodicity of properties in the periodic table :

Increasing the atomic number

Increasing:

- The atomic radius.
- The metallic property. (In groups start by a metal).
- The acidic property (In groups start by a nonmetal).
- The basic property (In groups start by a metal).

Decreasing:

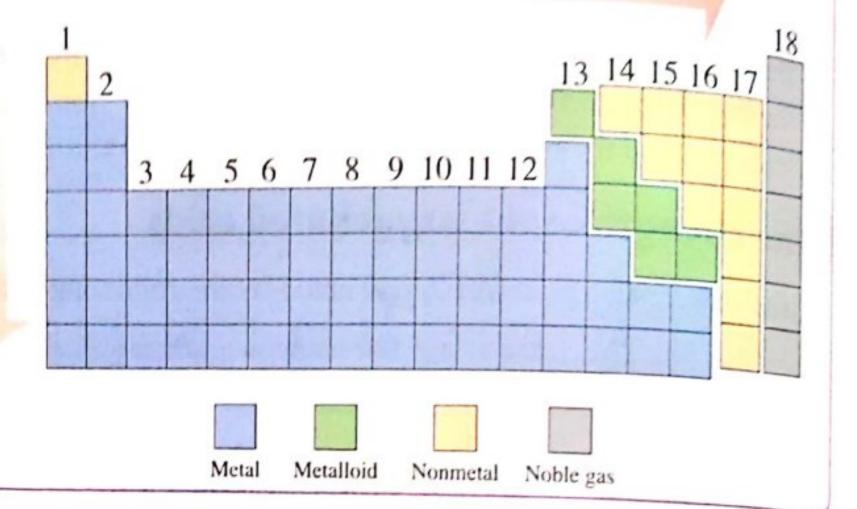
- The ionization potential.
- The electronegativity.
- The electron affinity.
- The nonmetallic property.

Increasing:

- The ionization potential.
- The electronegativity.
- The nometallic property.
- The acidic property of oxygenated acids.
- The electron affinity.

Decreasing:

- The atomic radius.
- The metallic property.
- The basic property.



Oxidation numbers

Oxidation number

It is a number that refers to the electric charge (positive or negative) that the atom or ion would have in the compound, whether it is an ionic or a covalent compound.

• The advantage of using oxidation numbers is that they can help us in determining the type of chemical change occurring to an element during the chemical reaction.

The significance of oxidation numbers:

The significance of oxidation numbers differs in ionic compounds from that of the covalent compounds.

In ionic compounds	In covalent compounds
If the oxidation number is	nositive it indicate
lost to give positive ion (cation).	- The electronic shift in the chemical bond between the atoms is away from the less electronegative sta
- The number of all	man-1!
The number of electrons that the atom has gained to give negative ion (anion).	- The electronic shift in the chemical bond between the atoms is toward the most electronegative atom.

Rules for calculating the oxidation numbers



Rules			App	plicati	on			
The oxidation number of the element atom in the								
molecule of similar atoms equals zero, whatever the	1	Element mol	ecule	Na	Cl_2	03	P ₄	S ₈
atoms. GR. Because the electronic shift in the bonds between the		Oxidation number of element atom Zero						
The oxidation number for element ion equals the		Ion		Cu ²⁺	Fe ³ -		O ²⁻	N ³⁻
charge (valence) of the ion.	0	xidation no.	+1	+2	+3			
The oxidation number for polyatomic ions (atomic groups) equals the charge	Atomic group	(NH ₄) ⁺ Ammonium H		(NO ₃) Nitrate gp.	Car	O ₃) ^{2 –} bonate gp.	(SO ₄) Sulpha	ate Pno
of group.	Oxidatio no.	n +1	-1	-l		-2	-2	
The oxidation number of any metal in: - Group 1A elements equals +1	C	compound m			3	MgSC +2	D ₄ A	1Cl ₃
- Group 2A elements equals +2 - Group 3A elements equals +3		Oxidation	no.	+1				
The oxidation number of fluorine in all of its		Compound n	olecule	Н	F	KF		NaF
compounds equals –1 GR. Because its electronegativity is greater than that of all		Oxidation	no.			-1		
other elements. The oxidation number for			219 548					
chlorine, bromine, iodine (halogens) in the most of		Compound n	olecule	Lie	CI	NaB	r	KI
their compounds equals (-1), however their other		Oxidation				-1		
oxidation numbers can be calculated mathematically (as will be viewed later).		_0 . T fee		tagin.		16 11		



0	The oxidation number
	of oxygen in most of its
	compounds is -2 , while its
	oxidation number in:

	**		1	1 1
4	Perox	ides	equa	15 -1

	1.00	1
* Sup	eroxides equals -	1/2

4	Its compound with
	fluorine equals +2

Oxide	Normal oxide	Per	oxide	Super- oxide	With fluoring
Formula	Na ₂ O	H_2O_2	Na ₂ O ₂	KO ₂	OF ₂
Oxidation no.	-2	-	-1	$-\frac{1}{2}$	+2

0	The oxidation number of
	hydrogen in most of its
	compounds is +1, except
	in binary compounds with
	active metals which are
	known as active metal
	hydrides, its oxidation
	number is -1

Molecula	HCl	NaH	CaH ₂	AlH ₃
Oxidation no.	+1	-1	-1	-1

Active metal hydrides

They are ionic compounds formed from the combination of an active metal with hydrogen in which hydrogen has an oxidation number -1 (negative ion).

1 The algebraic sum of the
oxidation numbers of the
different atoms in the
molecule equals zero.

In sodium chloride molecule NaCl:

The oxidation no. of Na (+1) + The oxidation no. of

$$C1 (-1) = zer_0$$

The algebraic sum of the oxidation numbers of the atomic groups forming the molecule equals zero.

In the molecule $[NH_4]^+[NO_2]^-$:

The oxidation no. of ammonium group (+1) + The oxidation no. of nitrite (-1) = zero

The algebraic sum of the oxidation numbers of the different atoms in a polyatomic ion equals the charge of ion (atomic group).

In hydroxide group OH⁻:

The oxidation no. of oxygen (-2) + The oxidation no.

of hydrogen (+1) = -1

Some elements, especially the transition elements have several oxidation numbers which can be calculated by knowing the oxidation numbers of the other known elements.

Give reason :

Hydrogen gas evolves at the anode (positive) in electrolysis of molten sodium hydride, while in electrolysis of acidified water, it evolves at the cathode (negative). Because the oxidation number of hydrogen in NaH molecule equals -1, while in H₂O molecule equals +1

How to assign the oxidation number of an unknown element in a given compound or atomic group:

Procedures	Application (1)	Application (2)
Write the oxidation number for each known element above its atom symbol in the compound molecule or atomic group formula.	1+ ? 2- K ₂ Cr ₂ O ₇	$(\overset{?}{C}\overset{2-}{O_3})^{2-}$
Multiply the oxidation number of each element by the number of its atoms in the molecule.	K_2 Cr_2 O_7 (-2×7)	$(CO_3)^2$ – (-2×3)
Assign the oxidation number of unknown element according to :		
 The algebraic sum of the atoms of the different elements in the molecule equals zero. The algebraic sum of the atoms of the different elements in the atomic group equals the charge of the group. 	$2 + 2Cr - 14 = 0$ $2Cr = +12$ $\therefore Cr = +6$	C + (-6) = -2 C = 6 - 2 C = +4

Example

Calculate the oxidation number of:

- 1 Chlorine in : (a) Cl₂
- **(b)** KClO₄
- ② Sulphur in : (a) $(SO_4)^{2}$
 - (b) $Na_2S_2O_3$
- **1** Chromium : $Cr_2(SO_4)_3$
- O Nitrogen in: $(NH_4)^+(NO_2)^-$

Solution

 $\mathbf{0}$ (a) 2Cl = 0

$$\therefore$$
 Cl = 0

- (b) $KClO_4^{1+?}$, $1 + Cl + (-2 \times 4) = 0$, Cl 7 = 0 : Cl = +7
- (a) $(SO_4)^{?2-2-}$, $S + (-2 \times 4) = -2$, S = 8-2 : S = +6
- (b) $Na_2S_2O_3$, $(1 \times 2) + 2S + (-2 \times 3) = 0$, 2S = +4 : S = +2
- $\overrightarrow{O} \overset{?}{\text{Cr}}_2(\overset{2-}{\text{SO}}_4)_3$, $2\text{Cr} + (-2 \times 3) = 0$, 2Cr = +6 : Cr = +3

- (NH₄)⁺(NO₂)⁻ is an ionic compound which consists of two atomic groups, the oxidation number of nitrogen in each of them is different.
 - $(NH_4)^+$, N+4=+1, N=1-4

- \therefore N = -3
- $(NO_2)^-$, N-4=-1, N=4-1 $\therefore N=+3$

Calculating the change of the oxidation number in the oxidationreduction reaction (redox reaction)

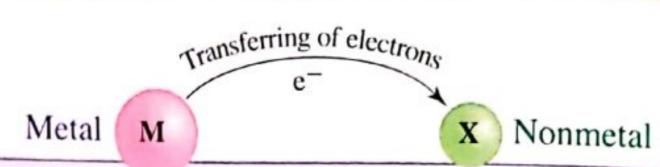
You already know the concepts of the oxidation and reduction, which are:

Oxidation

It is the process of losing electrons resulting in an increase of the positive charge.

Reduction

It is the process of gaining electrons resulting in a decrease of the positive charge.



In the chemical reaction

The metal loses one or more electrons. So, its oxidation number increases.

i.e. It is oxidized (oxidation process).

The nonmetal gains one or more electrons. So, its oxidation number decreases.

i.e. It is reduced (reduction process).

So, we can determine the changes happen to the elements during the oxidation-reduction reactions through the change in their oxidation no. before and after the reaction, where: • The reducing agent (metal) is oxidized. • The oxidizing agent (nonmetal) is reduced.

Reduction: decreasing the oxidation no.

$$-7$$
 -6 -5 -4 -3 -2 -1 0 $+1$ $+2$ $+3$ $+4$ $+5$ $+6$ $+7$

Oxidation: increasing the oxidation no.

Oxidation and reduction processes are accompanied by a change in the oxidation numbers

Example 1

Mention which of the following changes represents an oxidation or a reduction process and which change neither represents oxidation nor reduction:

$$\bigcirc$$
 CO₂ \longrightarrow CO

$$0 N_2O_4 \longrightarrow NO_2$$

Solution

$$C + (-2 \times 2) = 0$$

$$C = +4$$

$$C = +2$$
Reduction process

• Reduction process occurred to carbon as its oxidation no. decreased from +4 to +2

$$(Clo^{2})^{2} \longrightarrow (Clo^{3})^{2}$$

$$Cl + (-2) = -1$$

$$Cl + (-2 \times 3) = -2$$

$$Cl = +1$$

$$Cl = +4$$
Oxidation process

• Oxidation process occurred to chlorine atom as its oxidation no. increases from +1 to +4

$$\begin{array}{cccc}
& ? & 2 - & ? & 2 - & \\
N_2 & O_4 & \longrightarrow & NO_2 \\
2N + (-2 \times 4) = 0 & N + (-2 \times 2) = 0 \\
N = +4 & N = +4 \\
& & No \text{ change}
\end{array}$$

 No oxidation or reduction occurred, because there is no change in the oxidation number of nitrogen.

Example 2

Explain the type of change (oxidation or reduction) that occurred to iron and carbon in the following reaction:

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

Solution

$$\begin{array}{ccc}
? & 2- & 0 \\
Fe_2O_3 & \longrightarrow & Fe
\end{array}$$

$$2Fe + (-2 \times 3) = 0$$

$$2Fe = +6$$

$$\therefore Fe = +3 & Fe = 0$$
Reduction process

Reduction process occurred to iron, where the oxidation number of iron decreases from +3 to 0

$$\begin{array}{ccc}
\stackrel{?}{CO} & \longrightarrow & \stackrel{?}{CO}_2 \\
C + (-2) = 0 & C + (-2 \times 2) = 0 \\
C = +2 & C = +4 \\
\hline
Oxidation process
\end{array}$$

Oxidation process occurred to carbon, because the oxidation number of carbon increases from +2 to +4

Example 3

Explain the change of the oxidation and reduction that occurred for each of chromium and iron in the following reaction:



Solution

Reduction process occurred to chromium, because the oxidation number of chromium decreases from +6 to +3

$$\begin{array}{ccc}
? & 1-\\
FeCl_2 & \longrightarrow & ? & 1-\\
FeCl_3 & & & \\
Fe + (-1 \times 2) = 0 & & Fe + (-1 \times 3) = 0
\end{array}$$

Fe =
$$+2$$
 Fe = $+3$ Oxidation process

Oxidation process occurred to iron, because the oxidation number increases from +2 to +3

Example 4

Explain the change of the oxidation and reduction that occurred for sulphur in the following reaction, then mention the oxidizing agent and the reducing agent :

$$2H_2S + SO_2 \longrightarrow 2H_2O + 3S$$

Solution

$$H_2^{1+} \stackrel{?}{S} \longrightarrow S$$

$$(2 \times +1) + S = 0$$

$$S = -2 \qquad S = 0$$
Oxidation process

Oxidation process occurred to sulphur as its oxidation no. increases from -2 to 0

$$\begin{array}{ccc}
? 2-\\
SO_2\\
S + (-2 \times 2) = 0\\
S = +4\\
Reduction process
\end{array}$$

Reduction process occurred to sulphur as its oxidation no. decreases from +4 to 0

∴ SO₂ is an oxidizing agent, while H₂S is a reducing agent.

Example 5

Deduce the values of "n" from the following reactions:

(1)
$$S^{6+} + ne^{-} \longrightarrow S^{2-}$$

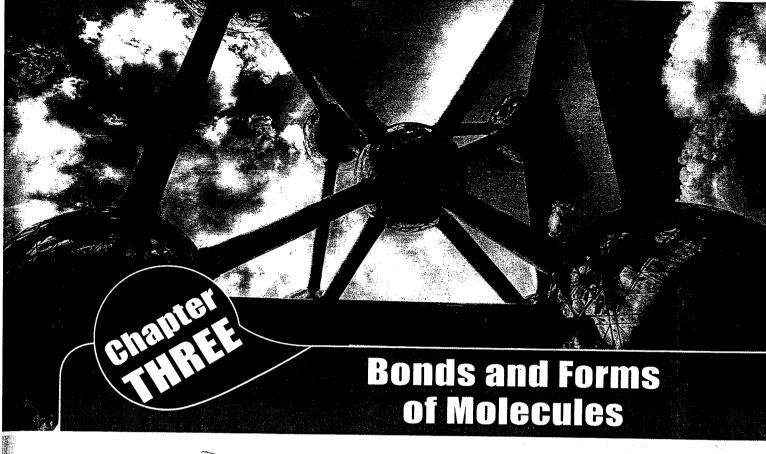
$$(2) 2Br^{n} - 2e^{-} \longrightarrow Br_{2}$$

Solution

$$(1) 6 + (n \times -1) = -2$$
, $6 - n = -2$

$$\therefore$$
 n = +8

(2)
$$2n - (2 \times -1) = 0$$
 , $2n + 2 = 0$, $2n = -2$





From The chemical combination.



Types of covalent bond.



From) Theories explaining the covalent bond.



The sigma and pi-bonds.

Lesson

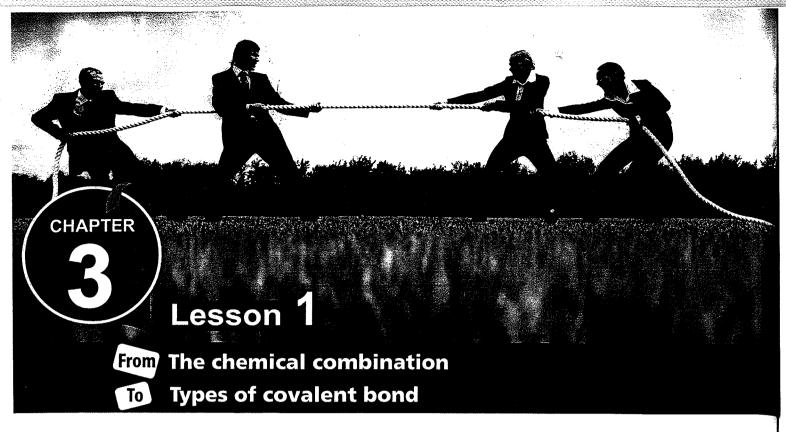
From/ The coordinate bond.

To The metallic bond.

General objectives of the Chapter

By the end of this Chapter, the student will be able to :

- Construe why atoms tend to form chemical bonds.
- Describe ionic and covalent bonds.
- Define the type of bond on the basis of electronegativity.
- Recognize the electronic theory of valence.
- Explain the inadequacies of the octet rule.
- Recognize the formation covalent bond in hydrogen and hydrogen fluoride molecules on the basis of the valence bond theory.
- Recognize the concept of hybridization.
- Explain the overlap of hydrogen and carbon orbitals to form methane molecules.
- Recognize the molecular orbital theory.
- Define shapes of molecules on the view of valence's electron pairs repulsion theory.
- Compare between sigma and pi bonds.
- Compare the type of hybridization of carbon atom in methane, ethylene and acetylene.
- Define the donor and the acceptor atoms in the coordinate bond.
- Recognize the hydrogen bond.
- Draw a diagram to explain the hydrogen bonds formed between water and hydrogen fluoride molecules.
- Conclude the melting point and the hardness of metals according to their valence electrons.



Chemical reaction concept

You have previously studied that:

• The most stable atoms are those of noble gases such as helium, neon, argon ... etc. **GR.** Because their outermost energy level is completely filled with electrons, as shown in the following table :

Noble gas	Electronic structure
Helium ₂ He	$1s^2$
Neon ₁₀ Ne	$[_{2}He] 2s^{2}, 2p^{6}$
Argon ₁₈ Ar	$[_{10}\text{Ne}] 3\text{s}^2, 3\text{p}^6$
Krypton 36Kr	$[_{18}Ar] 4s^2, 3d^{10}, 4p^6$
Xenon ₅₄ Xe	$[_{36}\text{Kr}] 5\text{s}^2, 4\text{d}^{10}, 5\text{p}^6$
Radon ₈₆ Rn	$[_{54}$ Xe $]$ 6s 2 , 4f 14 , 5d 10 , 6p 6

Mathematical Therefore:

- The atoms of these elements do not undergo any chemical reaction (under normal conditions) with other elements or with each other.
- Their molecules are monoatomic.
- All of the other elements are reactive to some extent. They undergo chemical reactions to complete their outermost shell by accepting, losing or sharing a number of electrons to acquire an identical electron configuration as that of the nearest noble gas.
- As the result of this change in the number of electrons in outermost shells of atoms, bonds are formed between atoms or bonds are broken to form new bonds, this is called a chemical reaction.

Chemical reaction

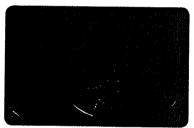
It is the breaking of bonds between atoms of the reactants molecules to form new bonds between atoms of the products molecules.

Application On the chemical reaction concept:

- The mixture of iron filings with sulphur powder is not considered a chemical compound. **GR.**Because there is no chemical reaction occurs between them.
- If this mixture is heated to a high temperature, a chemical reaction occurs (formation of chemical bond) between iron and sulphur producing the compound iron (II) sulphide.



The mixture properties are the same as that of its components



The compound properties differ than that of its components

Lewis electron-dot symbols

The valence electrons have an important role in the nature of the formed bond. So, the scientist Lewis had set a simple way to represent the valence electrons by using dots, as shown the following table:

Group	1A	2A	3A	4A	5A	6A	7A	0
Third period	₁₁ Na	₁₂ Mg	₁₃ Al	14Si	₁₅ P	₁₆ S	₁₇ Cl	₁₈ Ar
The electron configuration	[₁₀ Ne],3s ¹	[₁₀ Ne],3s ²	[₁₀ Ne],3s ² ,3p ¹	$[_{10}\text{Ne}],3\text{s}^2,3\text{p}^2$	[₁₀ Ne],3s ² ,3p ³	[₁₀ Ne],3s ² ,3p ⁴	[10Ne],3s ² ,3p ⁵	[₁₀ Ne],3s ² ,3p ⁶
Lewis electron- dot symbols	Na	•Mg•	· Al ·	· Si ·	• P •	· S ·	: Cl •	:Ar:

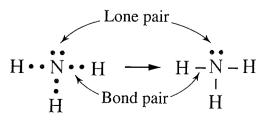
• The scientist Lewis had differentiated between the lone pair and bond pair of electrons.

Lone pair

The electron pair which is found in one of the outer orbitals and doesn't share in bond formation.

Bond pair

The electron pair which is responsible for the bond formation.



Dot representation for ammonia molecule

CHAPTER 3

Example

Redraw the structure of the opposite hydrazine molecule, showing the Lewis electron-dot is (lone and bond pair).

H H H N N H

Solution

$$_{1}H:1s^{1}$$
 $_{7}N:1s^{2},2s^{2},2p^{3}$
 $_{\bullet}H$
 $_{\bullet}H$
 $_{\bullet}H$
 $_{\bullet}H$



> Types of bonds

Bonds are divided into:

- **A** Chemical bonds:
- 1 Ionic bond.
- 2 Covalent bond.
- **3** Coordinate bond.

- **B** Physical bonds:
- **1** Hydrogen bond.
- 2 Metallic bond.

A Chemical bonds:

lonic bond

• This bond is usually formed between the elements of the two terminals of the periodic table which are :

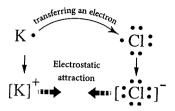
Metals	Nonmetals				
They are characterized by their large atomic volumes and their low ionization energies.	They are characterized by their small atomic volumes and their high electron affinities.				
The	refore				
Their atoms tend to lose the electrons	Their atoms tend to gain electrons (those				
of the outermost shell and change	lost by metal atoms) and change into anions				
into cations with an identical electron	with an identical electron structure to the				
structure to the noble gas preceds them	noble gas follows them in the periodic table.				
in the periodic table.					
Consequently, an electrostatic attraction					
occurs between the positive cations and the					
negative anions which i	s known as the ionic bond.				

• The ionic bond has no materialistic existence.

Application

The ionic bonding in potassium chloride molecule KCl:

Potassium metal
₁₉K: [
$$_{10}$$
Ne], $3s^2$, $3p^6$, $4s^7$



Chlorine nonmetal
$$_{17}$$
Cl: [$_{10}$ Ne], $3s^2$, $3p^5$

Example

Illustrate by drawing Lewis electron-dot symbol method, how is the combination between sodium and chlorine to form NaCl formula unit.

Solution

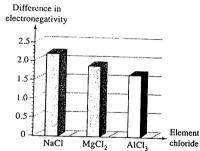
$$_{11}$$
Na: $[_{10}$ Ne], $3s^1$, $_{17}$ Cl: $[_{10}$ Ne], $3s^2$, $3p^5$
Na· + · Cl: \longrightarrow [Na] $^+$ [:Cl:] $^-$

The ionic bonding and the electronegativity

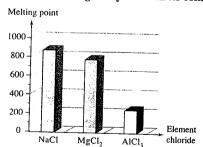
• The properties of ionic compounds differ according to the difference in electronegativity between their elements as shown in following table:

Group	1A	2A	3A			
Element	Sodium 11Na	Magnesium 12Mg	Aluminum 13 ^A l			
Electronegativity	0.9	1.2	1.5			
Chloride compound	NaCl	MgCl ₂	AlCl ₃			
Difference in electronegativity "electronegativity of chlorine = 3"	3 - 0.9 $= 2.1$	3 - 1.2 = 1.8	3 – 1.5 = 1.5			
Melting point	810°C	714°C	190°C			
Boiling point	1465°C	1412°C	Sublimates			
Electrical conductivity for molten chloride	Very Good conductor	Good conductor	Does not conduct			

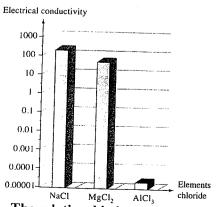
• It is clear from the previous table that the difference in electronegativity between the bonded elements plays a role in the characteristics of the ionic bond, where as the horizontal distance between the bonded elements - in the periodic table - increases, the difference in electronegativity increases, then the strength of ionic bond increases.



The relationship between elements' chlorides and the difference in electronegativity between its components



The melting points of the elements' chlorides



The relationship between elements' chlorides and their electrical conductivity

• In general, when the difference in electronegativity is more than 1.7 then the formed compound is ionic.

The ionic bond

It is the chemical bond which is formed between metals and nonmetals, the difference in electronegativity between them is more than 1.7

Give reasons:

- Molten sodium chloride conducts electricity more than molten magnesium chloride.

 Because the ionic bond in NaCl is stronger than that of MgCl₂ where the difference in electronegativity between sodium and chlorine is greater than that between magnesium and chlorine atoms.
- Although chlorine is a nonmetal and aluminum is a metal, aluminum chloride shows the properties of the covalent compounds.
 Because the difference in electronegativity between aluminum and chlorine atoms is less than 1.7
- 3 Sodium chloride has high melting and boiling points.

 Due to the strong ionic bond between sodium and chlorine atoms which is resulted from the high difference in electronegativity between them (2.1).

2 Covalent bond

• The covalent bond is usually formed between atoms of the same electronegativity (atoms of the same element) or of close electronegativity by sharing of electrons, where each atom shares by a certain number of electrons of the outermost shell equals the number of electrons required to complete this shell, forming a pair or more of electrons being in the vicinity of each atom.

Classification of covalent bond:

- The covalent bond is classified according to the difference in electronegativity between the bonded atoms into three types, which are:
 - 1 Pure covalent bond. 2 Non-polar covalent bond. 3 Polar covalent bond.

1 Pure covalent bond :

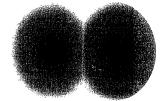
• When the two bonded atoms are of the same nonmetal element (have the same electronegativity):

Each atom in the molecule has the same ability to attract the two shared electrons (electron pair) of the bond, thus the electron pair spends the same time in the vicinity of each atom and the net charge for each of them equals zero. It is described as a pure covalent bond.

Pure covalent bond

It is the bond formed between two atoms, the difference in electronegativity between them equals zero.

- (1) The bond in hydrogen molecule (H H).
- (2) The bond in the fluorine molecule (F F).



Pure covalent bond

Non-polar covalent bond :

• When two atoms of different nonmetal elements are bonded, where the difference in electronegativity between them is greater than zero till 0.4. It is described as a non-polar covalent bond.

Non-polar covalent bond

It is the bond formed between two atoms of two different nonmetal elements, the difference in electronegativity between them is greater than zero till 0.4

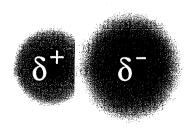
a cinida

The bond in methane molecule (C - H).

$\begin{array}{c|c} 2.5 & \swarrow & 2.1 \\ C - H \\ \text{Difference in electronegativity} \\ 2.5 - 2.1 = 0.4 \end{array}$

1 Polar covalent bond :

When the difference in electronegativity between the bonded atoms of two nonmetal elements is somewhat high (greater than 0.4 and less than 1.7), the more electronegative atom has a greater attraction for the electron pair of the bond. So, the electrons spend more time in the vicinity of it. As a result, the atom acquires a partial negative charge (δ⁻) - not a complete one - and because of this unequal sharing of the electron pair towards it, the less electronegative atom acquires a partial positive charge (δ⁺). The produced molecule is then described as a polar molecule and the bond is described as a polar covalent bond.



Polar covalent bond

CHAPTER 3

Polar covalent bond

It is the bond formed between two atoms of nonmetal elements, the difference in electronegativity between them is greater than 0.4 and less than 1.7

• As the difference in the electronegativity between the bonded elements in the polar molecule increases, the strength of the covalent bond increases.

क्षिता ।

The bond in hydrogen chloride molecule.

$$\delta^+$$
 $\delta^ H \rightarrow Cl$:

The bond in water molecule.

The bond in ammonia molecule.

Application The polar covalent bond in the hydrogen chloride molecule HCl:

• In hydrogen chloride molecule the more electronegative chlorine atom has a greater attraction for the electron pair of the covalent bond. So, the electron pair spends more time in the vicinity of the chlorine atom.

• As a result, the chlorine atom acquires a partial negative charge (δ^-) . Because of this unequal sharing of the electron pair towards chlorine, the hydrogen atom acquires a partial positive charge (δ^+) .

 $\begin{array}{cccc}
\delta^{\dagger} & & \delta \\
H & & Cl \\
\text{Hydrogen chloride}
\end{array}$

Hydrogen chloride molecule

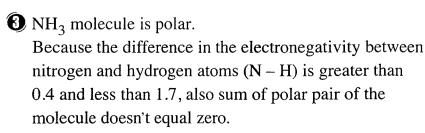
Give reasons:

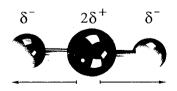
The bond in water molecule is polar covalent, while in chlorine molecule is pure covalent bond.

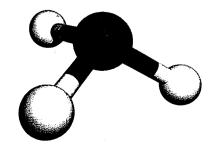
Because the difference in the electronegativity between the hydrogen and oxygen atoms in water molecule is somewhat high (greater than 0.4 and less than 1.7), while the difference in the electronegativity between the two chlorine atoms in chlorine molecule equals zero.

2 CO₂ gas is a nonpolar molecule, although it contains two polar bonds.

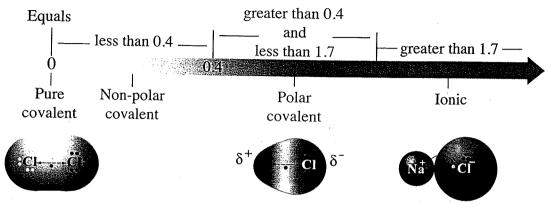
Due to the linear shape of its molecule which leads to cancelling the polar effect of bond by the other polar bond [sum of polar pair (di pole) moment = zero].







A summary of the relation between the difference in the electronegativity and bonds type :



The difference in electronegativity

Elemne

Determine type of the following covalent bonds, then arrange them ascendingly according to their polarity with giving reason.

 $(H-Cl),\,(C-O)$, (H-H) , (N-O) , $(P-Cl),\,(C-H)$ knowing that the electronegativity of their elements is as following :

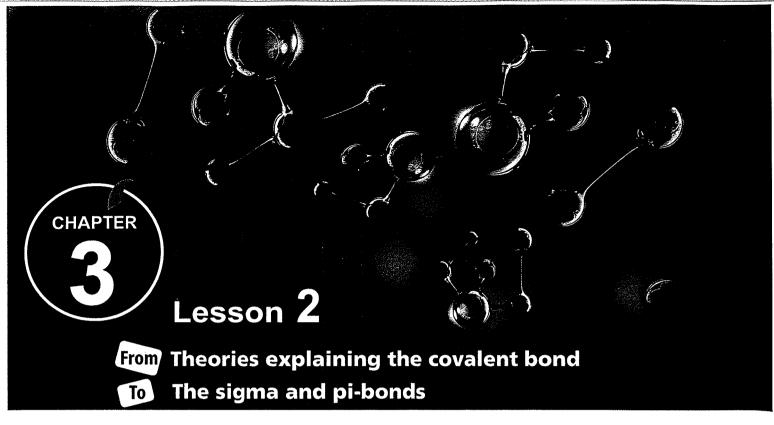
$$[H = 2.1, Cl = 3, C = 2.5, O = 3.5, N = 3, P = 2.1]$$

Solution

The bond	The difference in electronegativity	Type of the bond
H – Cl	3 - 2.1 = 0.9	Polar
C – O	3.5 - 2.5 = 1	Polar
H - H	2.1 - 2.1 = zero	Polar
N – O	3.5 - 3 = 0.5	Polar
P-Cl	3 - 2.1 = 0.9	Polar
C – H	2.5 - 2.1 = 0.4	Non-polar

$$\therefore$$
 (H - H) < (C - H) < (N - O) < (H - Cl) = (P - Cl) < (C - O)

When the difference in electronegativity between the bonded elements in the polar molecule increases, the strength of the covalent bond increases.



Theories explaining the covalent bond

The concept of the covalent bond developed according to our knowledge about the electron properties.

From the theories that are explaining the formation of the covalent bond are:

- The electronic theory of valence.
- **2** The valence bond theory.
- 3 The molecular orbitals theory.

1 The electronic theory of valence (octet rule 1916)

This theory was proposed by Lewis and Kosel, where they postulated that the covalent bond is formed when a number of electrons from the outermost shell of the two bonded atoms are shared between nuclei. Consequently, the outermost shell of each atom contains eight electrons through the sharing of electron pairs.



G.N. Lewis

Octet rule

With the exception of hydrogen, lithium and beryllium, the atoms of all elements tend to reach the octet structure of the nearest inert gas.

Application

Molecules in which the octet rule is applied:

Molecule	Electron configuration of atoms	Dots structures of molecules
Chlorine molecule (Cl ₂)	₁₇ Cl : [₁₀ Ne] , 3s ² , 3p ⁵	:Ci:Ci:
Water molecule (H ₂ O)	$_{8}^{O}: 1s^{2}, 2s^{2}, 2p^{4}$ $_{1}^{H}: 1s^{1}$	н:о:н
Ammonia molecule (NH ₃)	$_{7}^{N}: 1s^{2}, 2s^{2}, 2p^{3}$ $_{1}^{H}: 1s^{1}$	H:N:H H

The inadequacies of octet rule

The bonding in many molecules cannot be explained on the basis of the octet rule as in:

Phosphorus pentachloride molecule PCl ₅	Boron trifluoride molecule BF ₃	
$_{15}P:[_{10}Ne], 3s^2, 3p^3$	$\int_{5} B: 1s^{2}, 2s^{2}, 2p^{1}$	
$_{17}\text{Cl}:[_{10}\text{Ne}], 3\text{s}^2, 3\text{p}^5$	$_{5}B: 1s^{2}, 2s^{2}, 2p^{1}$ $_{9}F: 1s^{2}, 2s^{2}, 2p^{5}$	
CI CI CI P CI	·F····································	
Because		
The phosphorus atom is surrounded by	The boron atom is surrounded by only	
ten electrons.	six electrons.	

2 The simple representation of the covalent bond as being just a shared pair of electrons, is not sufficient to explain many of the properties of molecules such as the stereostructure and the angles between bonds.

CHAPTER 3

2 The valence bond theory

- This theory was based on the conclusions of quantum mechanics that considers the electron not only as a negative particle that moves in a definite orbit, but as a material particle with wave property which can exist in any position in the space surrounding the nucleus.
 This theory explains the formation of the covalent bond as a result of the overlap of an atomic orbital of one atom which contains a single electron with a similar orbital of another atom.
- The valence bond theory depends on two main concepts which are :
 - ① Overlapped orbitals concept.
 - (B) Hybridized orbitals concept.

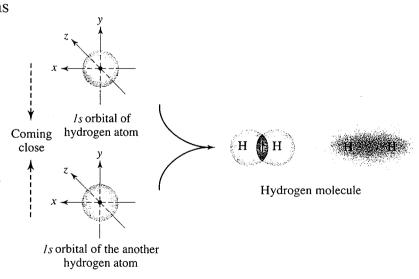
A Overlapped orbitals concept:

When two atoms come close to form a covalent bond, an atomic orbital of one atom - contains a single electron - overlaps with a similar orbital of another atom.

Application 1

The formation of hydrogen molecule according to the concept of the overlapped orbitals.

• When the two hydrogen atoms come close to each other, an overlapping occurs between 1s orbital (contains a single electron) of one atom with another 1s orbital (contains a single electron) of the other hydrogen atom to form the hydrogen molecule H₂



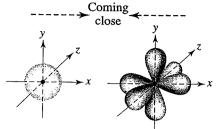
Application 2

The formation of hydrogen fluoride according to the concept of overlapped orbitals.

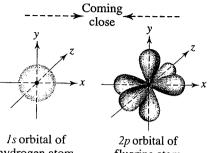
• When the fluorine atom comes close from the hydrogen atom, one of the 2p orbitals of the fluorine atom (which has a single electron) overlaps with the electron of 1s orbital (which has a single electron) of the hydrogen atom to form hydrogen fluoride molecule HF.

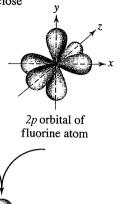
Hydrogen

H: 1s¹ $1s^1$





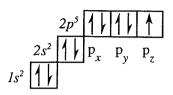






Fluorine

F: $1s^2$, $2s^2$, $2p^5$



Hydrogen fluoride molecule

The failure of the overlapped orbitals concept to explain the structure of methane molecule

- It is clear from the electron configuration of carbon that the ground state of the carbon atom has only two electrons in single state in 2p orbital.
- However, according to the overlapped orbital concept the carbon atom is bonded with two hydrogen atoms by two covalent bonds from the type of (C - H), in this way the formula of the methane molecule is – postulated – CH_2 and its bond angle equals 180° .
- But, on studying the bonds in the methane molecule actually it is found that the carbon atom is bonded with four hydrogen atoms by four symmetrical bonds in length and strength and the molecule takes the tetrahedron shape and the angles between its bonds = 109.5°
- The valence bond theory explained the formation of four covalent bonds in methane molecule by the excitation process which takes place when the carbon atom acquires a given amount of energy, then one electron from 2s orbital transfers to the vacant 2p orbital. Thereby, the carbon atom has four orbitals and each orbital contains a single electron. So, the carbon atom binding with 4 hydrogen atoms by 4 covalent bonds (C – H).



- But another problem is shown, the nonequivalence of the four (C H) bonds because the electron of the 2s orbital differs from the three electrons of the three 2p orbitals in energy and in the stereostructure of the orbitals.
- Thereby, the valence bond theory could not explain the structure of methane molecule in the light of the overlapped orbitals concept.

B The hybridized orbitals concept:

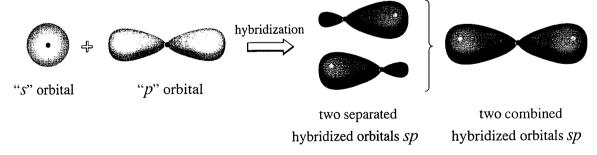
To solve the problem of the unsymmetry of the four orbitals in the excited carbon atom, there must be a further chance that occurs to the atomic orbital in the carbon atom resulting in the formation of four equivalent orbitals known as hybridized orbitals. This process is termed hybridization.

Hybridization

It is the process of the overlapping between two different orbitals or more of the same atom to produce a number of new equivalent orbitals called hybridized orbitals.

The conditions of the hybridization process:

- 1. It occurs between orbitals of the same atom.
- 2. It occurs between the orbitals of close energy e.g. (2s with 2p), (4s with 3d).
- 3. The number of the hybridized orbitals = the number of pure orbitals undergoing hybridization with their symbols



The hybridized orbital protrudes to the outside than the pure atomic orbital

Give reason :

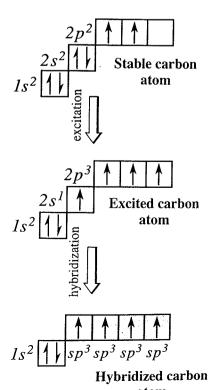
The hybridized orbitals are different in shape and more active than the pure orbitals. Because the hybridized orbitals are more protrusive to the outside so they are more capable of overlapping than the pure atomic orbitals.

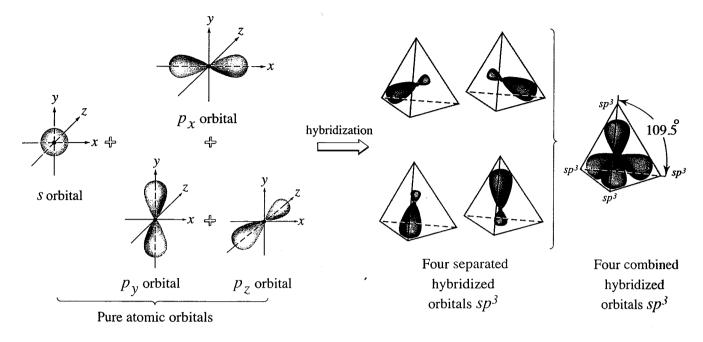
\bigstar The following table shows some of the hybridization types.

Hybridization type	Overlapping orbitals
sp ³	"s" orbital overlaps with three of "p" orbitals forming four hybridized orbitals, each of them is named sp^3 hybrid orbital. $s + 3p \xrightarrow{\text{hybridization}} 4sp^3$
sp ²	"s" orbital overlaps with two of "p" orbitals forming three hybridized orbitals, each of them is named sp^2 hybrid orbital. $s + 2p \xrightarrow{hybridization} 3sp^2$
sp	"s" orbital overlaps with one of the "p" orbital forming two hybridized orbitals, each of them is named sp hybrid orbital. $s + p \xrightarrow{hybridization} 2sp$

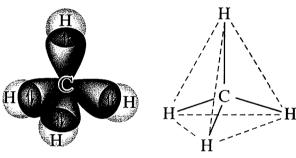
The explanation of the structure of methane molecule using the hybridized orbitals concept :

- The excitation process takes place when the carbon atom acquires a given amount of energy, then the carbon atom is said to be in an excited state.
- The four orbitals 2s, 2p_x, 2p_y and 2p_z are hybridized forming four hybrid orbitals, where each of them is named sp³ and contains one single electron.
- To overcome the repulsive forces between the orbitals, they are directed apart in space as far as possible till the angles between the hybrid orbitals become 109.5° then they will be more stable (less repulsive).





The carbon atom binds with four hydrogen atoms by overlapping of the four sp³ hybridized orbitals of carbon atom with four 1s orbitals of the four hydrogen atoms, forming the four symmetrical covalent bonds (C − H) in length and strength. The molecule takes the tetrahedron shape with angles between the bonds = 109.5°



Methane molecule CH_4 "tetrahedron shape"

3 The molecular orbital theory

- The valence bond theory considered the formation of covalent bonds in the molecule as a result of the overlap of some atomic orbitals in the combined atoms, the rest of the atomic orbitals which did not take part in the formation of bonds remain as they were in the free atoms.
- However, the molecular orbitals theory considered the molecule as one unit (or a big atom with multinuclei) in which all the atomic orbitals of the combined atoms are mixed or hybridized forming molecular orbitals, which have the symbols : sigma (σ) , pi (π) and delta (δ) .

A The sigma bond (σ)

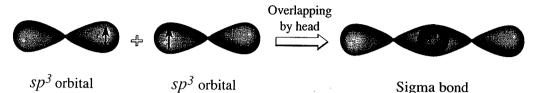
Sigma bond

The bond that is formed as a result of the overlap of two atomic orbitals along an axis by head to head.

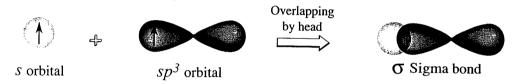
i.e. The overlapped orbitals are on one line or "collinear overlap".

EHamples

The overlap of the sp³ hybrid orbital of one atom with the sp³ of another atom.



2 The overlap of hybrid sp^3 orbital of one atom with the s orbital of another atom.



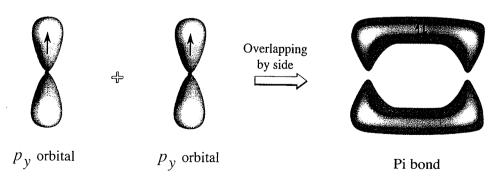
B The pi bond (π)

The pi bond (π)

The bond that is formed as a result of the overlap of two atomic orbitals side by side.

i.e. The overlap is between two parallel orbitals or "collateral overlap".

The overlap of the p_y atomic orbital of one atom side by side with its similar orbital in another atom (or p_z with p_z).



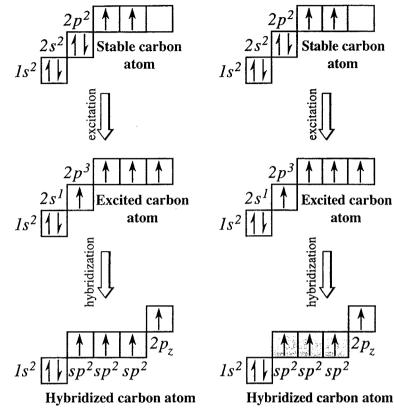
Give reason:

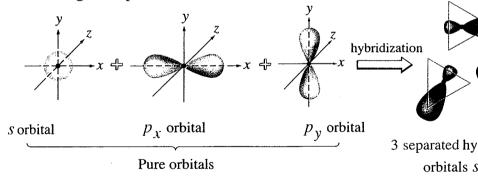
Sigma bond is stronger than pi bond.

Because sigma bond is formed from the overlapping between the hybrid orbitals together or with the atomic orbitals by head, while pi bond is formed from the overlapping of the atomic orbitals only by side.

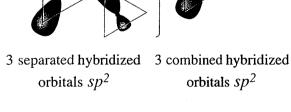
The explanation of the structure of ethylene molecule using the molecular orbital theory :

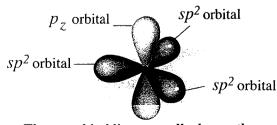
- The excitation process takes
 place for the two carbon atoms
 by acquiring the required amount
 of energy.
- After the two carbon atoms have been excited the three orbitals of 2s, 2p_x and 2p_y are hybridized forming three hybridized orbitals each of them is named sp² and contains one single electron. To overcome the repulsive forces between the orbitals, they are directed in space as far apart as possible, thus the angles between them are 120°. The atom then will be more stable and the molecule takes the planar triangle shape.





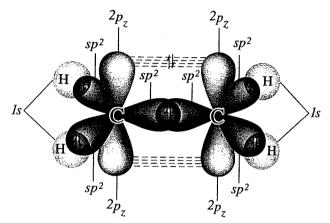
- It is observed that the $2p_z$ orbital of each carbon atom is not involved in the hybridization process. These two orbitals lie perpendicular on the plane of the three $2p^2$ hybrid orbitals of each carbon atom.
- There are two types of the overlapping between carbon atoms and two types of bonds are formed which are:





The p_Z orbital lie perpendicular on the plane of the sp² orbitals

- The sigma bond (σ) which is formed as a result of the overlap by head to head between :
 - Two sp² hybrid orbitals of each carbon atom with two 1s orbitals of the two hydrogen atoms, forming the two C H bonds.
 - The third sp^2 orbital of one carbon atom with the similar one on the other carbon atom forming the C-C bond.
- The pi bond which is formed as a result of the overlap side by side between :
 - The two $2p_z$ orbitals of the two carbon atoms forming the C-C bond between the two carbon atoms.



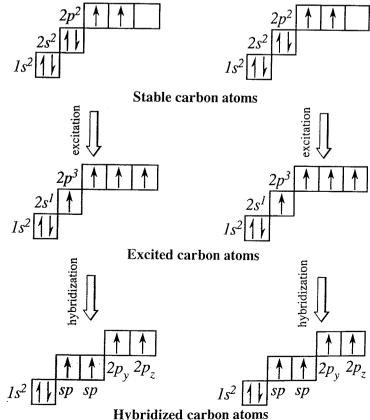
Formation of sigma and pi bonds in ethylene molecule

$$\begin{array}{ccc}
H & \sigma & \sigma & H \\
C & \sigma & C & H \\
H & G & G & H
\end{array}$$

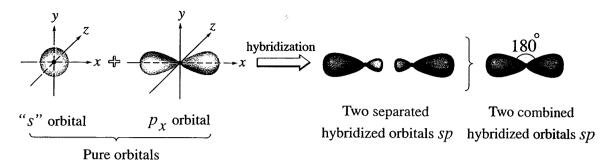
Ethylene molecule

The explanation of the structure of acetylene molecule using the molecular orbital theory :

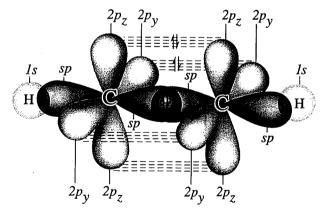
- It is clear that after the excitation process has occurred in the two carbon atoms by acquiring the required amount of energy, hybridization occurs between one orbital 2p_x from the sublevel (p) orbitals and the 2s orbital producing two sp hybridized orbitals, each one of them contains one single electron.
- To overcome the repulsive forces between the two hybridized orbitals, they are directed in space as far apart as possible, forming an angle of 180°. The atom then will be more stable and the molecule takes a linear shape.



CHAPTER 3



- It is observed that in each carbon atom there are two atomic orbitals remaining, i.e. $2p_y$ and $2p_z$ are not involved in the hybridization process.
- The two carbon atoms are bonded together and with hydrogen atoms by two types of bonds as the following:
- The sigma bond (σ) produced from the "head to head" overlap between :
 - One sp orbital of each carbon atom forming the C C bond between the two carbon atoms.
 - The remaining sp orbital of each carbon atom with the 1s atomic orbital of each hydrogen atom forming the C H bond for each carbon atom.
- The pi bond (π) produced from the side by side overlap between:
 - \bullet One p_y orbital of each carbon atom forming the (C-C) bond between the two carbon atoms.
 - One p_z orbital of each carbon atom forming the (C C) bond between the two carbon atoms.



$$H \stackrel{\overline{Q}}{=} C \frac{\overline{u}}{\underline{Q}} C \stackrel{\overline{Q}}{=} H$$

The formation of sigma and pi bonds in the acetylene molecule

Acetylene molecule

The valence shell electron pair repulsion (VESPR) theory

VESPR theory

The shapes of molecules differ according to (free and bonded) electron pairs which are found in the orbitals of the central atom in the covalent molecule or distributed in the space around the central atom of the molecule, where the repulsion between them is the minimum to form the most stable shape of the molecules.

It is observed according to the theory that :

• The lone pairs of electrons control the values of the angles between the bonds of the molecule, **GR.**

where the lone pair is bonded to the nucleus of the central atom from one side and spreads to the space from the other side.

- The bond pair is bonded from both sides to the two bonded atoms.
- Increasing the number of the lone pairs of electron in the central atom of the molecule leads to increasing the repulsive force between them. So, the angles between the covalent bonds of the molecule decreases.
- The repulsion force between (lone pair lone pair) > (lone pair bond pair) > (bond pair bond pair).

Shapes of the covalent molecules according to VESPR theory

The following table shows the molecular shapes, where:

A: is the central atom in the molecule.

X: is the atom bonded to the central atom.

E: is the lone electron pair.

Example of	Shape of the solid part	Arrangement of	F	Electron pa	airs
particles	(stereostructure)	electron pairs (lone and bond)	(free)	bonded	resultant
F — Be — F BeF ₂	linear AX_2	linear	0	2	2
BF ₃	Planar triangle AX_3	Planar triangle	0	3	3
SO ₂	Angular AX ₂ E Free electrons pair		1	2	

CH ₄ H C H H H	Tetrahedron AX ₄		0	4	
NH ₃	Three-base pyramid AX ₃ E	Tetrahedral	1	3	4
H ₂ O	Angular AX_2E_2	; -	2	2	·

- Suppose the stereostructure of the molecule which contains each of the following "by writing the abbreviations".
 - (a) 2 bond pairs, 0 lone pair.
 - (b) 3 bond pairs, 1 lone pair.

Solution

- (a) : The molecule contains 2 bond pairs.
 - :. It involves 2 covalent bonds.
 - : The molecule doesn't contain any lone pair and involves two covalent bonds.
 - \therefore The stereostructure of the molecule is linear and its abbreviation is AX_2

- (b) : The molecule contains 3 bond pairs.
 - : It involves 3 covalent bonds.
 - : The molecule contains 1 lone pair and involves three covalent bonds.
 - \therefore The stereostructure of the molecule is three-base pyramid and its abbreviation is AX_3E
- ② Conclude the number of bond pairs and lone pairs and the arrangement of the electrons pairs for the molecules which have the following abbreviations:
 - (a) AX_4

(b) AX₂E

Solution

(a) :: X = 4

- \therefore No. of bond pairs = 4
- : There is no value of E
- \therefore No. of lone pairs = 0
- : The total no. of the electron pairs = 4 + 0 = 4
- :. The arrangement of the electron pairs is tetrahedron.
- (b) :: X = 2

 \therefore No. of bond pairs = 2

:: E = 1

- \therefore No. of lone pairs = 1
- : The total no. of the electron pairs = 2 + 1 = 3
- .. The arrangement of the electron pairs is planar triangle.

Give reasons:

 \bullet SO₂ molecule is abbreviated as AX₂E, while H₂O molecule is abbreviated as AX₂E₂, although each of them consists of three atoms.

Because the central atom (A) in SO_2 molecule is bonded with two oxygen atoms (X_2) and carries one lone pair of electrons (E), while the central atom (A) in H_2O molecule is bonded with two hydrogen atoms (X_2) and carries two lone pair of electrons (E_2).

2 BeF₂ molecule is linear, while SO₂ molecule is angular, although the central atom in each of them is bonded to two atoms.

Because the central atom in BeF₂ molecule doesn't carry any lone pair of electrons, so the repulsion force between the two bond pairs is as large as possible which makes the linear stereostructure of the molecule.

While the central atom in SO₂ molecule carries lone pair of electrons which repulses strongly with the bond pair and this leads to reduce the angle value between them and makes the angular stereostructure of the molecule.

The stereostructure of ammonia molecule is three-base pyramid, while the arrangement of electron pairs in the same molecule takes tetrahedron shape. The stereostructure of ammonia molecule NH_3 is three-base pyramid because of bonding the central atom with three bond pairs, while the arrangement of the electron pairs in tetrahedron shape because the total number of electron pairs (bond and lone) equals 3 + 1 = 4

CHAPTER 3

Application

The relation between number of lone pairs of electrons and angles value between the covalent bonds in the molecule.

The following table shows the relation between the number of lone pairs of electrons and the angles value between the covalent bonds in each of methane, ammonia and water molecules.

The molecule	Methane (CH ₄)	Ammonia (NH ₃)	Water (H ₂ O)
Stereostructure	C C 109.5°	One lone electron pair	Two lone electron pairs 105°
No. of lone pair of electrons	0 <	 < 1 •	< 2
The angle between covalent bonds in the molecule	109.5°	 	> 105°

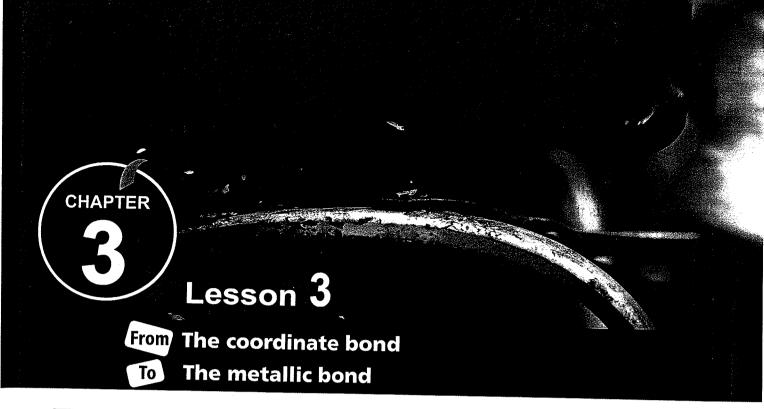
From the previous table, it is obvious that when the number of lone pairs of electrons in the central atom increases, the repulsion force increases, causing a decrease in the angles value between the covalent bonds in the molecule.

P Give reason:

The angle value between the covalent bonds in ammonia molecule is less than that in methane molecule.

Because the central atom in ammonia molecule carries one lone pair of electrons which repulses with the bond pairs and that leads to decreasing the angle value between them.

While the central atom in methane molecule doesn't carry a lone pair of electrons, so the angle value between the bond pairs is larger than that in ammonia molecule.



3 Coordinate bond

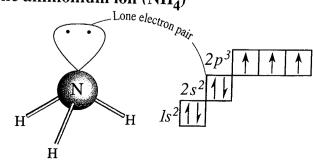
- The coordinate bond is a type of the covalent bonds which differs only in the origin of the electron pair which is shared between the atoms involved in the covalent bond. The electron pair forming the ordinary covalent bond is produced by both of the two combined atoms contributing one electron to the bond. Whereas the electron pair of the coordinate bond is produced only by one of the two combined atoms.
- The coordinate bond is formed between two atoms :
 - The first: having a lone pair of electron occupying one orbital. This atom is called the donor atom.
 - The second: having a vacant orbital, needing this electron pair to acquire the stable electron structure. This atom is called the acceptor atom.
- The coordinate bond is represented by an arrow directs from the donor atom to the acceptor atom.

The coordinate bond

It is the bond that is formed between a donor atom having a lone pair of electrons or more and an acceptor atom having a vacant orbital.

Application 1 The coordinate bond formed in the ammonium ion $(NH_4)^+$

- Ammonia gas dissolves in water forming a coordinate bond between :
 - Nitrogen atom of ammonia molecule which contains the lone pair of electrons. So, the nitrogen atom represents the donor atom.



Ammonia molecule

Nitrogen atom

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Water proton (positive hydrogen ion H⁺), which contains a vacant orbital accepts the lone pair of electrons from the nitrogen atom. So, the proton H⁺ represents the acceptor atom.

$$H^{+} + : N \stackrel{H}{\stackrel{\cdot}{\cdot}} H \longrightarrow \left[H \stackrel{\cdot}{\stackrel{\cdot}{\cdot}} H \stackrel{H}{\stackrel{\cdot}{\cdot}} H \right]^{+}$$

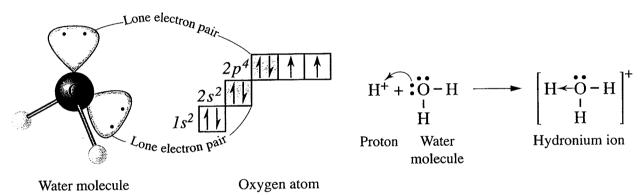
Proton Ammonia molecule

Ammonium ion

Formation of coordinate bond in ammonium ion

Application 2 The coordinate bond formed in the hydronium ion $(H_3O)^+$

- Acids dissolve in water forming the coordinate bond between:
 - Oxygen atom of water molecule which contains a lone electron pair. The oxygen atom represents the donor atom.
 - Acid proton (the positive hydrogen ion H⁺) which contains a vacant orbital accepts the lone electron pair from oxygen atom. The proton H⁺ represents the acceptor atom.



The formation of the coordinate bond in the hydronium ion

It is observed that the other lone electron pair remains as it is in the oxygen atom.

Give reasons:

There are no positive hydrogen ions (protons) in the aqueous solutions of the strong acids.

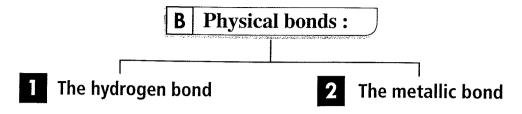
Because of their bonding with water molecules by coordinate bonds and forming hydronium ions (H_3O^+) .

$$H_2 O_{(\ell)} + H^+_{(aq)} \longrightarrow H_3 O_{(aq)}^+$$

2 Ammonium hydroxide molecule (NH₄OH) contains three types of the bonds.

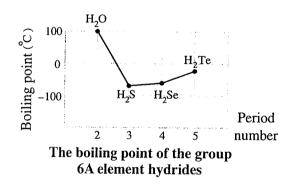
Because it contains:

- Ionic bond as a result of an electrostatic attraction occurs between the positive ammonium ion $(NH_A)^+$ and the negative hydroxide ion (OH^-) .
- Coordinate bond in ammonium ion, when the nitrogen atom of the ammonia molecule donates the lone electron pair to the proton H⁺
- Three covalent bonds in ammonia molecule resulting from the sharing of electrons between the nitrogen atom and the three hydrogen atoms.



1 The hydrogen bond

- It is known that water boils at 100°C. This temperature is considered to be high for a compound of a relative low molecular mass (18 g/mol).
- If this temperature is compared with the boiling point of hydrogen sulphide (of molecular mass 34 g/mol) which is 61°C, we will find a great difference although the oxygen precedes sulphur in the same group "6 A" in the periodic table.
- In general, as relative molecular mass increases, the boiling point increases, but the boiling point of water is anomalous in the group (VI) hydrides.
- This anomalousness of the boiling point of water is explained by the attraction of the water molecules to each other by what is known as the hydrogen bond or hydrogen bridge.
- To form the hydrogen bond, the hydrogen atom must becomes between two atoms of high electronegativity such as (N, O, F atoms).



The hydrogen bond

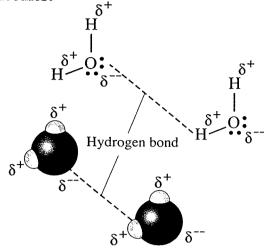
It is the bond that is formed between hydrogen atom binds by a polar bond [eg. : (F-H), (O-H), (N-H)] with high electronegative bonded atom [eg. : F, O, N].

• All the compounds of the hydrogen bonds are polar compounds dissolve in polar solvents as water.

- The bond between fluoride hydrogen molecules HF
- The bond between water molecules H₂O
- The bond between ammonia molecules NH₃

Application The hydrogen bonds between water molecules.

- The oxygen atom in water carries a partial negative charge (δ^{--}) .
- The two hydrogen atoms carry a partial positive charge (δ^+) .
- The hydrogen atom becomes as a bridge between the two oxygen atoms which are of a high electronegativity.
- The molecules get near to each other through the hydrogen atom which bonded the water molecules together.



The attraction of the water molecules through hydrogen bonds

Give reason:

The high boiling point of water.

Due to consuming of a big amount of heat energy to break the hydrogen bonds between water molecules.

The strength of hydrogen bond.

Although the hydrogen bond clearly affects physical properties of the compounds (as water), its bond strength is far weaker than the covalent bond. It is observed that as the length of the bond increases the bond strength becomes weaker.

	Bond length		Bond strength
Covalent bond	1 Å	>	418 kJ/mol
Hydrogen bond	3 Å	<	21 kJ/mol

• The strength of hydrogen bond increases when :

- The hydrogen bond becomes in a straight line with the polar covalent bond as in the water molecule H₂O and hydrogen fluoride molecule HF.
- By increasing the difference in the electronegativity between the hydrogen atom and the other atom in the polar covalent bond.

Solution Give reasons:

The hydrogen bonds in hydrogen fluoride molecule HF are stronger than that of water molecules.

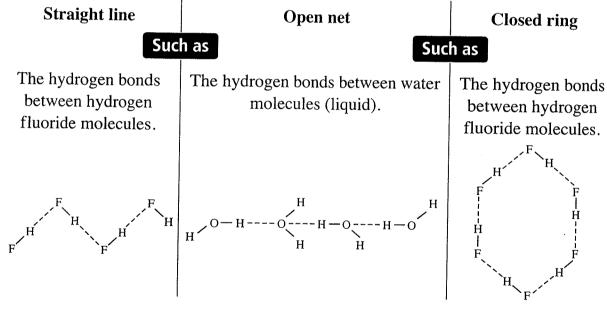
Because the difference in the electronegativity between fluorine and hydrogen is greater than that between oxygen and hydrogen and the strength of the hydrogen bond increases as the difference in the electronegativity between the bonded atoms increases.

The hydrogen bond between H₂O molecules is stronger than that between NH₃ molecules.

Because the difference in the electronegativity between oxygen and hydrogen atoms is greater than that between nitrogen and hydrogen atoms. In addition, the hydrogen bonds in water molecules are in a straight line with the polar covalent bond.

The forms of the compounds which have hydrogen bonds

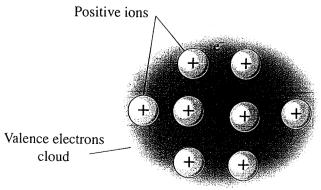
The compounds which have hydrogen bonds take several forms, the compounds may form:



2 The metallic bond

大学の主体に対するという。

• Each metal has a crystal lattice with a definite form in which the positive metal ions take a certain arrangement. The outermost shell electrons (valence electrons) of each atom are associated together forming an electron cloud with free movement to bind this great collection of positive metal ions by what is known as metallic bond.



Metallic bond in sodium metal "positive ions (cations) resembling brick molds and valence electron cloud as cement which binds molds together."

CHAPTER 3

• These free valence electrons account for the good electrical and thermal conductivity of metals.

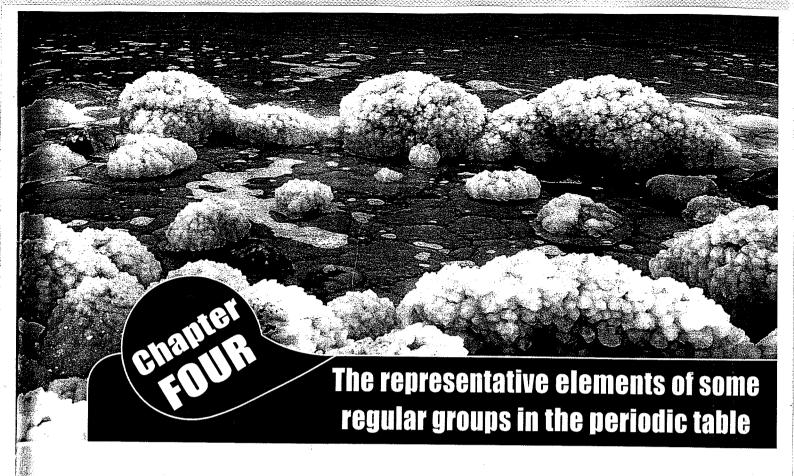
The metallic bond

The bond produced from the electron cloud of valence electrons which decreases the repulsive forces between the positive metal ions in the crystal lattice.

The metallic bond strength

- The number of valence electrons in the metal atom plays an important role in the strength of the metallic bond. As the number of valence electrons increases in the metal atoms, the atoms become more strongly bound and accordingly the metal becomes more hard and has a higher melting point.
- This is an evidence when comparing the properties of sodium, magnesium and aluminum (the metal of the third period), as the following table:

	Sodium ₁₁ Na	Magnesium ₁₂ Mg	Aluminum ₁₃ Al
The electron configuration	[₁₀ Ne], 3s ¹	$[_{10}Ne], 3s^2$	$[_{10}\text{Ne}]$, 3s^2 , 3p^1
Number of the outermost electrons	1	2	3
Hardness (Moh's scale)	Soft arough to be cut	Mild enough to be	Hard easily moulding
	Soft enough to be cut by a knife (0.5)	Mild enough to be bend (2.5)	(2.75)
Melting point °C	98°C	650°C	660°C



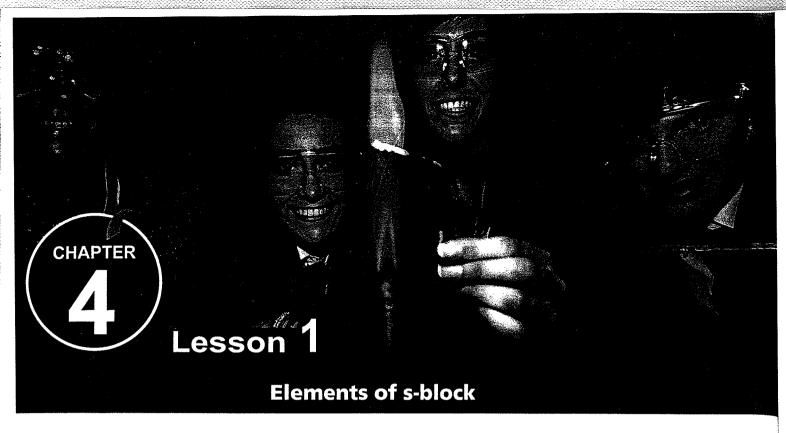
Lesson 1 Elements of s-block.

Lesson 2 Elements of p-block.

General objectives of the Chapter

By the end of this Chapter, the student will be able to :

- Recognize the alkali metals and their electronic configuration.
- Recognize the general characteristics of alkali metals.
- Conclude methods of extraction of alkali metals from their ores.
- Explain the general properties of sodium hydroxide.
- Practice some experiments for the identification of basic radicals.
- Describe the methods of preparation of sodium carbonate in both lab and industry.
- Recognize the general characteristics of the element of group five and their electronic configuration.
- Define the oxidation number of nitrogen in different compounds.
- Recognize methods of preparation of nitrogen gas in laboratory and its physical and chemical properties.
- Know how ammonia is prepared in laboratory and industry.
- Carry out an experiment to identify ammonia gas.
- Compare different types of nitrogenous fertilizers.
- Know how to prepare nitric acid in lab.
- Recognize the criteria of nitric acid.
- Distinguish between nitrate and nitrite salts.
- Know the economic importance of the fifth group elements.
- Consider safty rules in laboratory.
- Recognize scientist efforts in serving humanity.



• Elements of from our study of the periodic table, we have seen that one of the aims of the classification of elements in periods and groups is to facilitate their study in a regular way.

The regular groups concept

• In this chapter, we will study the representative elements in some of the regular groups. In these regular groups there is a great regularity and graduation in their properties, the property which is not found in the transition elements.

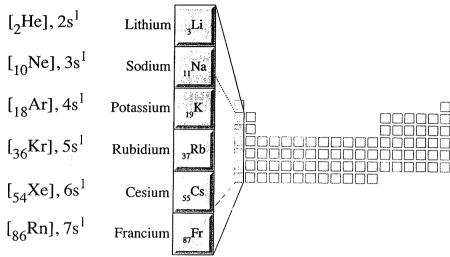
* We will study only from them:

- The metals of group 1A (from elements of s-block) >> In lesson one
- The elements of group 5A (from elements of p-block) ⇒ In lesson two

Elements of group 1A (Alkali metals):

- Elements of this group are known as alkali metals (forming alkalis). This naming returns to Moslem scientists, who gave the name "Al-Kale" to both sodium and potassium elements, this name was borrowed by Europeans, becoming "Alkali". Then, this word was used to encompass all elements of this first group.
- The alkali metals group comprises six elements:

Symbol and the atomic number



The position of the alkali metals group in the periodic table

Abundance of alkali metals in nature

☆ The most common abundant alkali metals are :

Sodium

Potassium

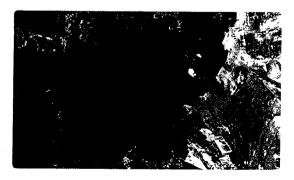
The order of their abundance in the Earth's crust

6th

7th

Their most important ores:

• Rock salt NaCl



Rock salt

- Potassium chloride KCl, which is found in:
 - Sea water.
 - Carnallite deposits (KCl.MgCl₂.6H₂O)



Carnallite

- Other metals of this group are rare,
 - e.g. francium.
 - It is a radioactive element which is a product of the disintegration of actinium:

$$^{227}_{89}$$
Ac \longrightarrow $^{223}_{87}$ Fr + $^{4}_{2}$ He

- The amount of francium formed in this decaying process is very small.

- All of what is known about it is:
 - a. its atomic number.
 - b. its approximate atomic mass.
 - c. its half life period is only twenty minutes.

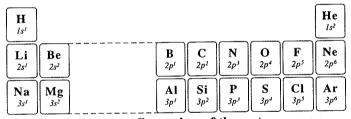
General properties of the first group elements (Alkali metals)

- The presence of a single electron in the outer energy level.
- Their atoms have the largest atomic volume.
- They give characteristics colors (atomic spectra) when the electron of these elements are excited to a higher energy level.
- 1 They react with atmospheric air.
- **5** They react with water.
- **6** They react with acids.
- They react with oxygen.
- 1 They react with nonmetals.
- Most of their oxygenated salts are thermally stable.

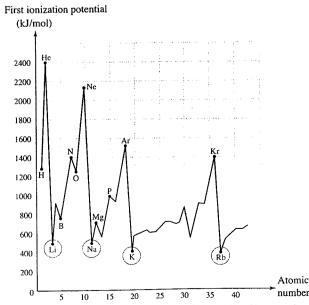
In the following, we shall offer a more detailed study of these properties :

1 The presence of a single electron in the outer energy level

- All elements of this group (1A) are characterized by the presence of one single electron in the outer energy level (ns¹), accordingly:
 - Each element of this group lies at the beginning of a new period in the periodic table.
 - The oxidation number of all group (1A) elements in their compounds is only (+1).
 - ① Due to the ease of losing of the valence electron they are chemically very active. So, the first ionization potential is less than the ionization potential of any other elements in the period.
 - The second ionization potential is very large. **GR.**Since the second electron will be removed from a complete or a saturated energy level (stable).



The electron configuration of the outer energy level of alkali metals is ns^t



Small ionization potential of the alkali metals

- They are strong reducing agents. **GR.**Because of its ability to lose the valence electron easily.
- 6 Most of their compounds are ionic, the ion of each element is identical in electronic structure to the noble gas which precedes it.
- Metals of the first group are characterized by a small attraction between their atoms and their weak metallic bonds **GR.** Since the number of electrons in the outer energy level in the metal atom is one of the factors which controls the strength of the metallic bond and these metals have only one electron in the outer energy level (valence orbit).

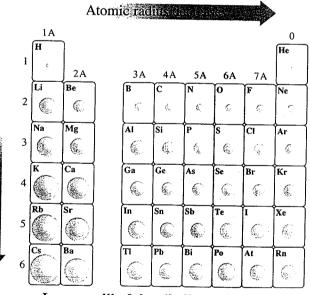


Sodium is a soft metal due to its weak metallic bond

So, they are the most malleable metals, with the lowest melting and boiling points.

2 Their atoms have the largest atomic volumes

- Any metal of this group has the largest atomic volume than any other atom in its period.
- The volume of the atom increases down through the group i.e. with increasing atomic number.
- Due to the increase in the volume in the atom, alkali metals show the following properties:
- The easily loss of the valence electron, as the increase in the atomic radius decreases the attraction force between the valence electron and the nucleus, therefore the alkali metals are considered the highest electropositive and chemical activity elements.
 - Due to their high chemical activity they must be kept away from air and humidity under the surface of liquid hydrocarbons such as kerosene.



Large radii of the alkali metal atoms



Sodium is stored under kerosene

2 Easy liberation of electrons from the outer surface of some alkali metals (as potassium & cesium) when they are exposed to light which is known as "photo-electric phenomenon". This is due to their large atomic volume and their small ionization energy. So, potassium and cesium are used in photo-electric cells.

The photo-electric phenomenon

It is the liberation of electrons from the outer surface of the alkali metals when they are exposed to the light.

- 1 Low densities.
- These elements have a very low electronegativity, compared with other elements when combining with other elements they form strong ionic bonds.

Give reason:

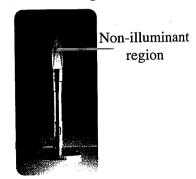
Cesium is used in photoelectric cells.

Because its radius is big and its ionization energy is very small. So, it is easy to liberate the valence electron when exposed to light.

3 Atomic spectra

- You have already learned that when the valence electrons of the element are excited to a higher energy level by heating or electrical discharge and then the excited electron comes back to the ground state, there is an emission of radiation of visible light occurs.
- Similarly, on exciting the electrons of these elements' ions to higher energy levels, they give different characteristic colors.
- This property is used in the dry test (flame test) of these elements in their compounds as the following:
- A platinum wire is dipped in a concentrated hydrochloric acid to clean it.
- 2 Dip the platinum wire in the unknown salt and expose it to the non-illuminant Bunsen flame.

The flame will acquire the characteristic color of the cation.



The non-illuminant region of Bunsen burner flame represents the over heat regions

Element	Lithium	Sodium	Potassium	Cesium
Cations	Li ⁺	Na ⁺	K ⁺	Cs ⁺
	Crimson	Golden yellow	Pale violet	Bluish violet
Color	9			

4 Action of atmospheric air

- All elements of this group are chemically active.
 They are oxidized easily in air to lose their metallic luster due to forming a layer of the oxide.
- Lithium can react with nitrogen of the atmospheric air by heating giving lithium nitride, which itself reacts with water to produce ammonia gas.

$$6\text{Li}_{(s)} + \text{N}_{2(g)} \xrightarrow{\Delta} 2\text{Li}_{3}\text{N}_{(s)}$$
 $\text{Li}_{3}\text{N}_{(s)} + 3\text{H}_{2}\text{O}_{(\ell)} \xrightarrow{} 3\text{LiOH}_{(aq)} + \text{NH}_{3(g)}$
lithium ammonia nitride gas



Sodium loses its metallic luster in air

5 Reaction of alkali metals with water

• Elements of this group are located at the top of the electrochemical series. So, they can replace the hydrogen of water and this reaction is accompanied by the liberation of a large amount of energy which leads to the burning of the hydrogen gas evolved.



Lithium with water



Sodium with water



Potassium with water

• The reaction becomes more vigorous down through the group where in the reaction of cesium, an explosion occurs.

The reaction of sodium with water.

$$2Na_{(s)} + 2H_2O_{(l)} \longrightarrow 2NaOH_{(aq)} + H_{2(g)}$$

Give reason :

Sodium fires are not put out by water.

Because sodium reacts strongly with water in an exothermic reaction which leads to the burning of the evolved hydrogen gas.

CHAPTER 4

6 Reaction of alkali metals with acids

• Alkali metals can replace the hydrogen in acids and this reaction is a vigorous reaction.

$$2Na_{(s)} + 2HCl_{(aq)} \longrightarrow 2NaCl_{(aq)} + H_{2(g)}$$

Reaction of alkali metals with oxygen

• The trend in activity in elements of this group is clear when it reacts with oxygen. When these elements are burnt in an atmosphere of oxygen, they give three types of oxides which are:

Normal oxide	Peroxide	Superoxide
Lithium gives lithium oxide "normal oxide" when it is burnt in an atmosphere of oxygen. $4Li_{(s)} + O_{2(g)} \xrightarrow{180^{\circ}C} 2Li_2O_{(s)}$	Sodium gives sodium peroxide when it is burnt in an atmosphere of oxygen. 2Na _(s) + O _{2(g)} → Na ₂ O _{2(s)}	Potassium, rubidium and cesium give superoxides when they are burnt in an atmosphere of oxygen.
	oxidation number of oxygen in	$K_{(s)} + O_{2(g)} \xrightarrow{300^{\circ}C} KO_{2(s)}$
(-2)	(-1)	(-1/2)

Reparation of oxides of the alkali metals:

The normal oxide of the alkali metals (M₂O) can be prepared by dissolving the metal in liquified ammonia and then adding a calculated amount of oxygen.

• (M refers to the symbol of the metal).

$$4M + O_2 \xrightarrow{\Delta} 2M_2O$$

• It is a strong basic oxide that reacts with water to give the strongest known alkaline solutions "except Li₂O".

Give reasons:

1 Potassium peroxide is used in purifying the air in submarines and planes. Because potassium superoxide reacts with carbon dioxide giving oxygen.

$$4KO_{2(s)} + 2CO_{2(g)} \xrightarrow{CuCl_2} 2K_2CO_{3(s)} + 3O_{2(g)}$$

- The peroxide and superoxide compounds act as strong oxidizing agent.
 - As the peroxide compounds react with acids and water, producing hydrogen peroxide.

$$Na_2O_{2(s)} + 2HCl_{(aq)} \longrightarrow 2NaCl_{(aq)} + H_2O_{2(\ell)}$$

 $Na_2O_{2(s)} + 2H_2O_{(\ell)} \longrightarrow 2NaOH_{(aq)} + H_2O_{2(\ell)}$

Additional information

 H_2O_2 decomposes easily into water and oxygen $2H_2O_{2(\ell)} \longrightarrow 2H_2O_{(\ell)} + O_{2(g)}$

Oxygen gas is responsible for making oxidation process.

- While the superoxide compounds react with water and acid, producing hydrogen peroxide and oxygen.

$$2KO_{2(s)} + 2HCl_{(aq)} \longrightarrow 2KCl_{(aq)} + H_2O_{2(\ell)} + O_{2(g)}$$

 $2KO_{2(s)} + 2H_2O_{(\ell)} \longrightarrow 2KOH_{(aq)} + H_2O_{2(\ell)} + O_{2(g)}$

Reaction of alkali metals with nonmetals

Alkali metals react with hydrogen giving hydrides, which are ionic compounds in which hydrogen has an oxidation number equals (-1).	$2\text{Li}_{(s)} + \text{H}_{2(g)} \xrightarrow{\Delta} 2\text{LiH}_{(s)} \qquad \text{lithium hydride}$ $2\text{Na}_{(s)} + \text{H}_{2(g)} \xrightarrow{\Delta} 2\text{NaH}_{(s)} \qquad \text{sodium hydride}$
Alkali metals react vigorously with halogens forming very stable ionic halides and the reaction is accompanied with an explosion.	$2Na_{(s)} + Cl_{2(g)} \longrightarrow 2NaCl_{(s)}$ sodium chloride $2K_{(s)} + Br_{2(\ell)} \longrightarrow 2KBr_{(s)}$ potassium bromide
with sulphur and phosphorus	$2Na_{(s)} + S_{(s)} \xrightarrow{\Delta} Na_2S_{(s)}$ sodium sulphide $3K_{(s)} + P_{(s)} \xrightarrow{\Delta} K_3P_{(s)}$ potassium phosphide

Give reason:

Hydride compounds act as reducing agents.

Because they react with water and hydrogen gas evolves where hydrogen gas is responsible for making reduction process.

$$LiH_{(s)} + H_2O_{(\ell)} \longrightarrow LiOH_{(aq)} + H_{2(g)}$$

- **?** The action of heat on alkali metal oxygenated salts
 - Alkali metal oxygenated salts are thermally stable.
 - a. All alkali metal carbonates do not decompose when heated, except lithium carbonate which decomposes at $1000^{\circ}\mathrm{C}$

$$\text{Li}_2\text{CO}_{3(s)} \xrightarrow{1000^{\circ}\text{C}} \text{Li}_2\text{O}_{(s)} + \text{CO}_{2(g)}$$

b. Alkali metal nitrates decompose partially giving metal nitrite and oxygen.

$$2\text{NaNO}_{3(s)} \xrightarrow{\text{heat}} 2\text{NaNO}_{2(s)} + O_{2(g)}$$

Give reasons:

1 Potassium nitrate is used in manufacturing of bombs.

Because it partially decomposes by heat and the reaction is accompanied with an explosion.

$$2KNO_{3(s)} \xrightarrow{heat} 2KNO_{2(s)} + O_{2(g)}$$

2 Sodium nitrate is not used in manufacturing of bombs.

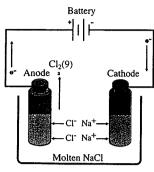
Because it is a deliquescent material that absorbs water vapor from the atmospheric air.

CHAPTER



Extraction of alkali metals from their ores

- These elements are not found in nature in a free state. but rather in the form of ionic compounds. GR. Because these metals easily lose their valence electron and they are the most powerful reducing agents.
- Preparing of these metals involves the electrolysis of its molten (fused) halide.



Electrolytic cell

Application Extraction of sodium metal from its ores:

- By the electrolysis of molten sodium chloride in the presence of a flux substance to decrease the melting point of the halide.
- Oxidation and reduction reactions occur at anode and cathode, as the following:

$$2Cl^{-} \xrightarrow{\text{oxidation}} Cl_2 + 2e^{-}$$
 (At anode)
 $2Na^{+} + 2e^{-} \xrightarrow{\text{reduction}} 2Na$ (At cathode)



Alkali metals compounds

From the commonly known sodium compounds:

① Sodium hydroxide NaOH

② Sodium carbonate Na₂CO₃

Sodium hydroxide NaOH

The most important properties of sodium hydroxide

- ① A white hygroscopic solid compound (absorbs water vapor from atmosphere).
- It has a soapy feel and corrosive effect on skin.
- 3 It dissolves easily in water forming an alkaline solution and the reaction is accompanied by the liberation of heat energy as it is an exothermic dissolution.
- It reacts with acids forming the sodium salt of the acid and water [Neutralization reaction].

$$\begin{aligned} &\operatorname{NaOH}_{(\operatorname{aq})} + \operatorname{HCl}_{(\operatorname{aq})} \longrightarrow \operatorname{NaCl}_{(\operatorname{aq})} + \operatorname{H}_2\operatorname{O}_{(\ell)} \\ &\operatorname{2NaOH}_{(\operatorname{aq})} + \operatorname{H}_2\operatorname{SO}_{4(\operatorname{aq})} \longrightarrow \operatorname{Na}_2\operatorname{SO}_{4(\operatorname{aq})} + \operatorname{2H}_2\operatorname{O}_{(\ell)} \end{aligned}$$



The most important uses of sodium hydroxide

- It is used in many important industries such as: Soap, synthetic silk and paper.
- ② It is used to purify petroleum from the acidic impurities.
- 1 It is used in detection of basic radicals (cations) such as Cu²⁺ and Al³⁺
- Detection of Cu²⁺ and Al³⁺ cations by using sodium hydroxide solution:

(a) Copper (II) cation Cu²⁺

(b) Aluminum cation Al³⁺

Detection

By adding sodium hydroxide solution to the cation solution

Such as copper II sulphate

Such as aluminum chloride

Observation

A blue precipitate of copper II hydroxide is formed which turns black on heating, due to forming of copper II oxide.

A white gelatinous precipitate of aluminum hydroxide is formed which dissolves in excess reagent (NaOH) to form sodium meta aluminate (NaAlO₂), which is soluble in water.



Blue precipitate of copper II hydroxide



Gelatinous white precipitate of aluminum hydroxide

Equations

$$CuSO_{4(aq)} + 2NaOH_{(aq)} \longrightarrow$$

$$Na_2SO_{4(aq)} + Cu(OH)_{2(s)} \downarrow$$
blue ppt.
$$Cu(OH)_{2(s)} \xrightarrow{heat} H_2O_{(\ell)} + CuO_{(s)} \downarrow$$

AlCl_{3(aq)} + 3NaOH_(aq)

$$3NaCl_{(aq)} + Al(OH)_{3(s)} \downarrow$$
white ppt.

Al(OH)_{3(s)} + NaOH_(aq)

$$NaAlO_{2(aq)} + 2H_2O_{(\ell)}$$
sodium meta
aluminate

2 Sodium carbonate Na₂CO₃

The most important properties of sodium carbonate

- White powder, easily dissolves in water and its solution has an alkaline effect.
- 2 It is thermal stable compound i.e. it melts by heat without decomposition.
- 1 It reacts with acids forming sodium salt of acid and carbon dioxide gas evolves.



Carbon dioxide evolves when sodium carbonate reacts with hydrochloric acid

$$Na_2CO_{3(s)} + 2HCl_{(aq)} \longrightarrow 2NaCl_{(aq)} + H_2O_{(l)} + CO_{2(g)}$$

The most important uses of sodium carbonate

• Manufacture of glass.

2 Paper industry.

Textile industry.

Water softening.

Preparation of sodium carbonate in laboratory

By passing carbon dioxide gas through a hot solution of sodium hydroxide then the solution is left to cool, white crystals of hydrated sodium carbonate are separated gradually.

$$2\text{NaOH}_{(aq)} + \text{CO}_{2(g)} \xrightarrow{\Delta} \text{Na}_2\text{CO}_{3(aq)} + \text{H}_2\text{O}_{(\ell)}$$

Note

2NaOH_(aq) + CO_{2(g)}
$$\xrightarrow{[H_2O]}$$
 Na₂CO₃ .10H₂O_(s) $\xrightarrow{\Delta}$ Na₂CO_{3(s)} + 10H₂O_(v) sodium carbonate

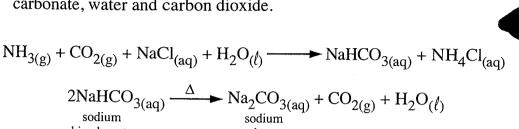
Give reason :

The hydrated sodium carbonate $Na_2CO_3.10H_2O$ is known as washing soda. Since it is used to remove the water hardness which is arised from the presence of soluble Ca^{2+} and Mg^{2+} salts in water. Where, washing soda reacts with these salts forming calcium carbonate and magnesium carbonate which are insoluble in water. So, the water hardness is removed as shown in the following equations:



Preparation of sodium carbonate in industry (Solvay process)

- By passing ammonia and carbon dioxide gases in a saturated aqueous solution of sodium chloride to produce sodium bicarbonate.
- Heating sodium bicarbonate, it will decompose to sodium carbonate, water and carbon dioxide.





Solvay



The biochemical role of sodium and potassium elements

Sodium ions	Potassium ions
They are considered the most abundant ions	They are considered the most abundant ions
present in :	present in the living cell.
- the blood plasma.	
- the intercellular fluids in the body.	

The biological role

They have an important role in the vital processes. GR. Because they represent the required medium to transfer the nutrients such as glucose and amino acids.

bicarbonate

They play an important role in: Oxidation of glucose in the living cell. GR. To produce the required energy for its activity.

The natural sources

- Vegetables (specially celery).
- Milk and its products.

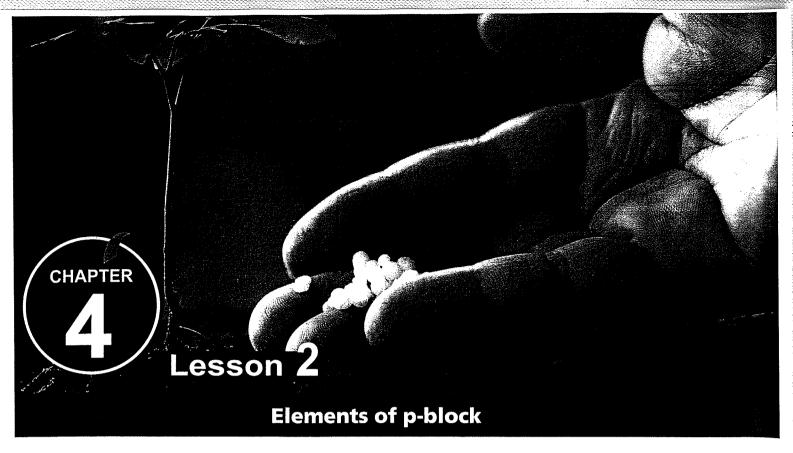


Natural sources of sodium

- Meat.
- Milk.
- Eggs.
- Vegetables.
- Cereals.

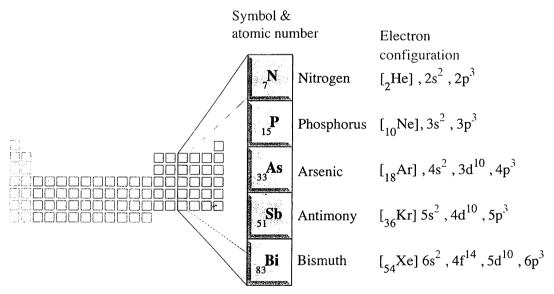


Natural sources of potassium



Group 5A (group 15)

This group consists of five elements which are:



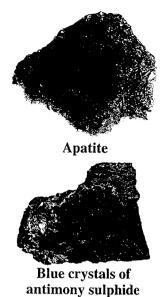
The position of group (5A) in the periodic table

Abundance of the elements of group 5A in nature

Elements of this group are not abundant in nature, except nitrogen which represents about 80% of atmospheric air ($\frac{4}{5}$ of air volume).

The following table illustrates the forms of these elements which are found in nature :

Element	The form found in nature
Phosphorus	1. Calcium phosphate
"It is the most abundant	$Ca_3(PO_4)_2$
element of this group in the	2. Apatite CaF ₂ .Ca ₃ (PO ₄) ₂
Earth's crust".	the salt of calcium fluoride
	and calcium phosphate.
Arsenic	Arsenic sulphide As ₂ S ₃
Antimony	Antimony sulphide Sb ₂ S ₃
Bismuth	Bismuth sulphide Bi ₂ S ₃



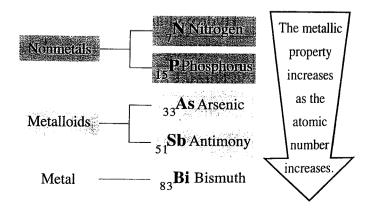
General properties of group 5A elements (group 15)

The properties of group 5A elements graduate regularly depending on the increase in atomic number and atomic size as illustrated in the following:

- Graduation of the metallic and non-metallic properties.
- **②** Different number of molecule atoms of each element.
- **3** Several oxidation numbers.
- **Q** Several allotropic forms.
- **1** The acidity of oxides.
- 1 The basicity of hydrides.

1 The graduation of the metallic and the nonmetallic properties

- The metallic property increases by increasing the atomic number (downward the group).
- The properties of this group elements tend to be those of the non-metals, even bismuth is a metal but its ability to conduct electricity is weak.





2 Different number of molecule atoms of group 5A elements

• The number of molecule atoms of each element of this group differs as the following :

Element	The number of atoms of the molecule	Symbol of molecule
Nitrogen	A molecule contains two atoms.	N ₂
Phosphorus	Their vapors have molecules which contain four atoms.	P ₄
Antimony		As ₄
Arsenic		Sb ₄
Bismuth	It forms a metallic crystal lattice and its vapor consists of diatomic molecules.	Bi ₂

Give reason :

Although bismuth is a metal, it has different properties than that of the other metals.

Because of its low electric conductivity relatively to other metals and it has a diatomic structure in the vapor state, whereas those of the other metals have monoatomic structure.

3 Several oxidation numbers

- Elements of this group are characterized by having several oxidation numbers in their different compounds from (-3) to (+5). **GR.**Because through covalent sharing they may:
 - gain till 3 electrons.
 - lose till 5 electrons.

\bigstar The following table shows the oxidation numbers of nitrogen in some of its compounds :

The compound	Formula	Oxidation no.
Ammonia	NH ₃	-3
Hydrazine	$(NH_2 - NH_2) N_2H_4$	-2
Hydroxyl amine	NH ₂ OH	-1
Nitrogen	N ₂	0
Nitrous oxide	N ₂ O	+1
Nitric oxide	(N ₂ O ₂) NO	+2
Nitrogen trioxide	N ₂ O ₃	+3
Nitrogen dioxide	NO ₂	+4
Nitrogen pentoxide	N ₂ O ₅	+5



Give reason :

The oxidation numbers of nitrogen in the oxygenated compounds are positive while that in the hydrogenated compounds are negative.

Because the electronegativity of nitrogen is less than that of oxygen and higher than that of hydrogen.

Several allotropic forms

Allotropy

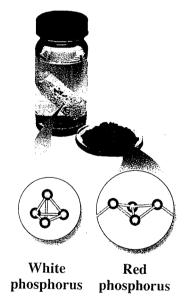
This is the presence of the element in more than one form which is of different physical properties, but of similar chemical ones.

• The allotropic phenomena appears in the solid nonmetals only. GR.

This is due to the presence of the solid nonmetal element in different crystalline forms, each form differs in the number of atoms and in their arrangement.

The following table shows some of the allotropic forms of the group 5A elements :

The element	Allotropic forms
Phosphorus	White (waxy), red, violet
Arsenic	Black, grey, yellow (waxy yellow)
Antimony	Yellow, black



Give reason :

Allotropy exists in phosphorus, but not in nitrogen and bismuth.

Because phosphorus is a solid nonmetal, while nitrogen is a gaseous nonmetal and bismuth is a metallic element, in which gases and metals don't have allotropic forms.

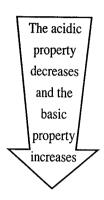
5 The acidity of oxides

- ullet All elements of this group form oxides have the formula : X_2O_3 , X_2O_5
- Some of these oxides are acidic, others are amphoteric and others are basic.

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• The basic property increases (the acidic property decreases) of these oxides with increasing of the atomic number, as shown in the following table:

Element	Its oxide	Type of oxide	
₇ N	N_2O_3 N_2O_5		
₁₅ P	P ₂ O ₃	Acidic oxide	
33As	As ₂ O ₃		
₅₁ Sb	Sb ₂ O ₃	Amphoteric oxide	
₈₃ Bi	Bi ₂ O ₃ Bi ₂ O ₅	Basic oxide	



6 The basicity of hydrides

• Most of the elements of this group react with hydrogen forming hydrides, the oxidation number of the element is −3 as in :

Ammonia NH₃

2 Phosphine PH₃

3 Arsine AsH₃

- The central atom in these compounds still has a lone pair of electrons in its valence shell (outer energy level). So, it can give this pair of electrons to other atoms or ions making coordinate bonds.
- Based on that, the basicity of the hydride depends on the ability of its central atom to lose one pair of electrons or gain a proton from another substance, ammonia is more basic than phosphine.

$$NH_3 + H_2O \longrightarrow NH_4^+ + OH^-$$

 $PH_3 + H_2O \longrightarrow PH_4^+ + OH^-$

The properties of hydride of the group 5A elements:

- Their thermal stability decreases. So, they decompose even by gentle heating.
- The **polarity** of hydrogen compounds in this group decreases with increasing atomic number of the element attached to hydrogen, thus:
 - Their solubility in water decreases.

Give reason:

The solubility degree of phosphine in water is less than that of ammonia. Because the polarity of phosphine is less than the polarity of ammonia.

The most famous elements in 5A group (nitrogen)

Nitrogen is considered as the most famous element in 5A group, in more details we will study the following:

- Its preparation in the lab.
- ② Its properties: (a) physical properties.
- (b) chemical properties.

1 Its famous compounds.

First Preparation of nitrogen gas in the lab.

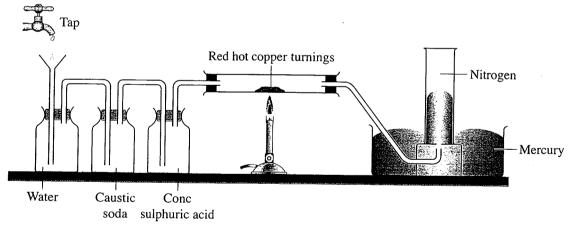
1 The main method (from the atmospheric air)

It can be prepared from the atmospheric air, by removing of:

- carbon dioxide.
- water vapor.
- oxygen gas.

By using the following apparatus:

It is the same steps followed in preparation of nitrogen gas in industry.



Preparation of nitrogen gas in laboratory from atmospheric air

The atmospheric air is passed through sodium hydroxide solution **GR.** to remove carbon dioxide gas.

$$2\text{NaOH}_{(aq)} + \text{CO}_{2(g)} \longrightarrow \text{Na}_2\text{CO}_{3(aq)} + \text{H}_2\text{O}_{(f)}$$

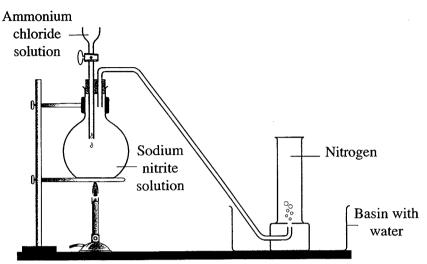
- Then it is passed through conc sulphuric acid GR. to absorb water vapor.
- 3 Finally it is passed over red hot copper turnings GR. to remove oxygen gas.

$$2Cu_{(s)} + O_{2(g)} \xrightarrow{\Delta} 2CuO_{(s)}$$

Nitrogen is collected by downward displacement of water or collected over mercury surface **GR.** to get dried.

2 From the chemical compounds

By heating a mixture of sodium nitrite and ammonium chloride solutions.



Preparation of nitrogen gas from two solutions of sodium nitrite and ammonium chloride.

$$\begin{array}{c} \text{NaNO}_{2(aq)} + \text{NH}_{4}\text{Cl}_{(aq)} & \xrightarrow{\Delta} & \text{NH}_{4}\text{NO}_{2(aq)} + \text{NaCl}_{(aq)} \\ & \xrightarrow{\text{NH}_{4}\text{NO}_{2(aq)}} & \xrightarrow{\Delta} & 2\text{H}_{2}\text{O}_{(\ell)} + \text{N}_{2(g)} \\ & \xrightarrow{\text{Dano}_{2(aq)}} + \text{NH}_{4}\text{Cl}_{(aq)} & \xrightarrow{\Delta} & \text{NaCl}_{(aq)} + 2\text{H}_{2}\text{O}_{(\ell)} + \text{N}_{2(g)} \end{array}$$

Give reason:

Nitrogen gas is collected during its preparation by downward displacement of water. Because nitrogen gas is lighter than water and sparingly soluble in it.

Second > The properties of nitrogen

A Physical properties

- Colorless, odorless and tasteless gas.
- 2 It is lighter than air GR. as air contains oxygen gas (32 g/mol) which is heavier than nitrogen (28 g/mol).
- 1 It is sparingly soluble in water $[23 \text{ mL}(N_2)/1\text{L} (H_2\text{O}) \text{ at STP}]$.
- 1 It has a neutral effect on litmus paper.
- 1 Its density is (1.25 g/L at STP).
- Its boiling point is (-159.79°C), i.e. it can be liquified at this temperature at normal atmospheric pressure.

B Chemical properties

The reactions of nitrogen gas with the other elements occur in the presence of an electric spark (550°C) or an electric arc (3000°C) or by strong heating ... **GR.**

Because of the difficulty of breaking the triple bond between the two nitrogen atoms in one molecule of it.

The following table shows the reaction of nitrogen with the other elements:

Hydrogen: By an electric spark (550°C) ammonia gas (NH ₃) is formed.	$N_{2(g)} + 3H_{2(g)} \xrightarrow{\text{electric spark}} 2NH_{3(g)}$
Oxygen: By an electric arc (3000°C), nitric oxide (NO) gas is formed which is instantly changing into (oxidized) nitrogen dioxide (NO ₂).	$N_{2(g)} + O_{2(g)} \xrightarrow{\text{electric arc}} 2NO_{(g)}$ $\text{Then } 2NO_{(g)} + O_{2(g)} 2NO_{2(g)}$
Metals: At high temperature, nitrogen reacts with metals like magnesium giving the metal nitride which easily decomposes in water and ammonia gas evolves.	$3Mg_{(s)} + N_{2(g)} \xrightarrow{\Delta} Mg_{3}N_{2(s)}$ $Mg_{3}N_{2(s)} + 6H_{2}O_{(\ell)} $ $3Mg(OH)_{2(aq)} + 2NH_{3(g)}$
Calcium carbide: By the electric arc, calcium cyanamide (CaCN ₂) is formed which is used as a fertilizer.	$CaC_{2(s)} + N_{2(g)} \xrightarrow{\text{electric arc}} 3000^{\circ}C$ $CaCN_{2(s)} + C_{(s)}$

Give reason:

Calcium carbide is used as a fertilizer.

Because it produces ammonia gas in the agricultural soil when the land is being irrigated.

$$CaCN_{2(s)} + 3H_2O_{(l)} \longrightarrow CaCO_{3(s)} + 2NH_{3(g)}$$

Third The most famous nitrogenous compounds

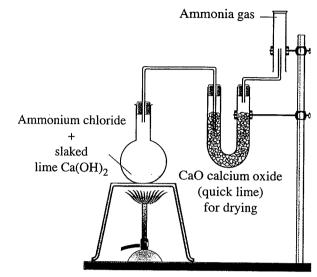
The most famous nitrogenous compounds are:

- **1** Ammonia NH₃
- **②** Nitric acid HNO₃

Ammonia NH₃

Preparation of ammonia in the lab.

- ① Set the apparatus as in the opposite figure.
- **2** Put in the flask a mixture of ammonium chloride NH₄Cl and calcium hydroxide (slaked lime) Ca(OH)₂
- Put a drying agent (quick lime CaO) in the U-shaped tube.
- Heat the contents of the flask, then collect the ammonia gas by downward displacement of air.



Preparation of ammonia in lab.

$$2NH_4Cl_{(s)} + Ca(OH)_{2(s)} \xrightarrow{\Delta} CaCl_{2(s)} + 2H_2O_{(\ell)} + 2NH_{3(g)}$$

Give reasons :

- Ammonia gas is collected by downward displacement of air. Because it is lighter than air.
- Conc. sulphuric acid is not used in drying ammonia gas when it is prepared in the lab. Because it reacts with ammonia gas and produces ammonium sulphate.

Preparation of ammonia gas in industry (Haber-Bosh method)

Ammonia gas can be prepared in industry from nitrogen and hydrogen, in the presence of a catalyst (iron, molybdenum), under 200 atmospheric pressure and 500°C.

$$N_{2(g)} + 3H_{2(g)} \xrightarrow{Fe/Mo \text{ Catalyst}} 2NH_{3(g)}$$

The properties of ammonia

- Colorless gas with a characteristics pungent smell.
- It does not burn readily or sustain combustion where the glowing splint is extinguished when approached it.
- 3 It is highly soluble in water forming an alkaline solution (ammonium hydroxide), it turns to blue color by adding few drops of litmus solution to it as shown in the following fountain experiment.

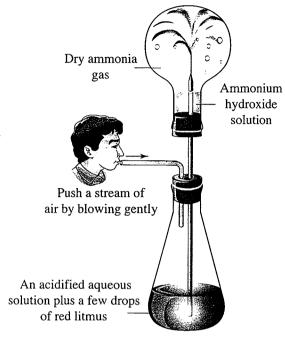
>> Fountain experiment

Procedures :

- **1** Build up the apparatus as shown in the opposite figure. Where,
 - The lower flask is filled with an acidified aqueous solution added to it a few drops of litmus solution. So, the color of the solution becomes red
 - The upper flask is filled with ammonia gas.
- A stream of air is blown to the lower flask.

Observation :

- Rushing out of the red solution from the lower flask to the upper flask in a form of fountain.
- **2** Changing the color of the red solution once it is rushed out in the upper flask into blue color.



The fountain experiment proves that:

- Ammonia gas is highly soluble in water.
- Its aqueous solution has an alkaline effect.

Conclusion :

- ① Rushing out of the solution of the lower flask in a form of fountain is an indication that ammonia is highly soluble in water.
- 2 Changing the color of the red solution into blue is an indication for the formation of a solution which has an alkaline effect on litmus solution (ammonium hydroxide).

$$NH_{3(g)} + H_2O_{(\ell)} \longrightarrow NH_4OH_{(aq)}$$



Give reason :

Ammonia gas is considered as a base anhydride. Because it reacts with water forming ammonium hydroxide (weak base).

Detection of ammonia gas

Ammonia gas forms dense white fumes of ammonium chloride (solid substance that sublimates) when subjected to a glass rod wetted with conc. hydrochloric acid.

$$NH_{3(g)} + HCl_{(g)} \longrightarrow NH_4Cl_{(s)}$$



Detection of ammonia gas

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For illustration

Sublimation is the change of the matter from a solid state to a gaseous state directly, without changing into liquid state.

The role of ammonia in the manufacturing of fertilizers

• Nitrogen is present in the soil in the form of inorganic and organic substances, it is considered one of the main sources of nutrition in plant **GR.** since it is an essential element to form protein.

However, the amount of nitrogen in the soil decreases by time. So, the soil should be enriched by nitrogen either by adding:

- Synthetic nitrogenous fertilizers.
- Natural fertilizers (manure).
- Although nitrogen forms about 4/5 of the air volume, plant cannot use it by a direct way in its gaseous form. Accordingly, it is a must to provide the soil by nitrogen in the form of ammonium salts or urea which dissolve in the irrigation water where they absorbed by the plant roots.
- Ammonia is considered the essential starting materials for manufacturing most of :
 - Nitrogenous fertilizers.
 - Nitrogenous phosphorus fertilizers.

Nitrogenous fertilizers

The inorganic nitrogenous fertilizers (ammonium salts) are synthesized by a neutralization reaction between ammonia and the suitable acid.

Some of the important inorganic nitrogenous fertilizers are :

a. Ammonium nitrate fertilizer	b. Ammonium sulphate fertilizer		
Preparation method			
By reacting ammonia with nitric acid NH _{3(g)} + HNO _{3(ℓ)} → NH ₄ NO _{3(aq)} Prop	By reacting ammonia with sulphuric acid $2NH_{3(g)} + H_2SO_{4(aq)} \longrightarrow (NH_4)_2SO_{4(aq)}$ erties		
 * It has a high nitrogen content (35%). * It is highly soluble in water. * An excess amount of it causes an acidic effect on the soil. 	* Continuous use of it increases the acidity of the soil, thus it is important to neutralize the soil by basic substances.		

🔯 Nitrogenous phosphorus fertilizers:

* They are prepared by reacting ammonia with phosphoric acid

$$3NH_{3(g)} + H_3PO_{4(aq)} \longrightarrow (NH_4)_3PO_{4(aq)}$$

* Nitrogenous phosphorus fertilizers (Ammonium phosphate) is an important fertilizer because it provides the soil with two essential elements which are nitrogen and phosphorus.

Give reason:

The slaked lime is added to the soil which is proved with ammonium sulphate fertilizers. To neutralize the soil, as ammonium sulphate acts to increase the soil acidity.

Notes on fertilizers:

- **①** Urea fertilizer:
 - It has a high nitrogen content (46%).
 - It is the most suitable fertilizer for hot are, **GR.** Where the high temperature increases its dissociation to ammonia and carbon dioxide.



Fertilizing the soil with urea

- **2** Anhydrous liquified ammonia fertilizer (future fertilizer).
 - It has the highest nitrogen content overall fertilizers (82%).
 - It is supplied to the soil in a depth of nearly 12 cm.



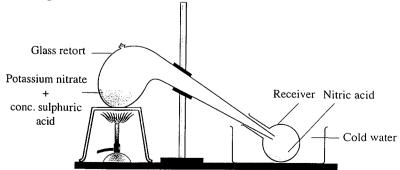


Liquified ammonia is supplied to the soil in a depth of nearly 12 cm

2 Nitric acid HNO₃

Preparation of nitric acid in the lab.

- **1** Set the apparatus as in figure.
- Put potassium nitrate and concentrated sulphuric acid in the retort and the receiver in a trough containing cold water.



Preparation of nitric acid in lab.

- Heat the contents of the retort gently but not to exceed the temperature 100°C.
- Collect the acid formed in the receiver.

$$2KNO_{3(s)} + H_2SO_{4(\ell)} \xrightarrow{conc} K_2SO_{4(aq)} + 2HNO_{3(\ell)}$$

The properties of nitric acid:

- 1 Colorless liquid.
- 2 It turns to red color when adding a few drops of litmus solution.
- 3 Strong oxidizing agent especially the concentrated acid and this is illustrated from:
 - a. The action of heat on it.
- b. Its action on metals.
- c. Passivity phenomena.

A The action of heat on nitric acid

It decomposes by heat giving brown fumes of nitrogen dioxide (NO₂). It is an oxidizing agent **GR**.

Because oxygen gas evolves as a result of its thermal decomposition.

$$4HNO_{3(\ell)} \xrightarrow{\Delta} 2H_2O_{(\ell)} + 4NO_{2(g)} + O_{2(g)}$$

B Action of the acid on metals

Nitric acid reacts with metals as an oxidizing agent and this is illustrated from the following:

The chemical reaction

- Nitric acid reacts with metals above hydrogen in the electrochemical series, giving metal nitrate and the atomic hydrogen which reduces the acid forming nitric oxide gas NO and water.
- Nitric acid reacts with metals below hydrogen in the electrochemical series. GR.

Because it is a strong oxidizing agent which combines with the metal forming a basic oxide which reacts with acid forming the salt of acid and water. The type of the produced gas differs according to the concentration of acid.

Illustrative examples

The diluted nitric acid reacts with iron forming iron (III) nitrate and liberating nitric oxide gas (colorless) which turns to reddish brown color at the top of the tube.

$$Fe_{(s)} + 4HNO_{3(aq)} \xrightarrow{\Delta} Fe(NO_3)_{3(aq)} + 2H_2O_{(\ell)} + NO_{(g)}$$

- The diluted nitric acid reacts with copper and liberating nitric oxide gas.

$$3Cu_{(s)} + 8HNO_{3(aq)} \xrightarrow{\Delta}$$

 $3Cu(NO_3)_{2(aq)} + 4H_2O_{(\ell)} + 2NO_{(g)}$

 When the conc. nitric acid is added to copper, brown vapor of nitrogen dioxide is formed and copper ions Cu²⁺ form green color in the solution.

$$Cu_{(s)} + 4HNO_{3(\ell)} \xrightarrow{\Delta} Cu(NO_3)_{2(aq)} + 2H_2O_{(\ell)} + 2NO_{2(g)}$$



Reaction of copper with conc. nitric acid

C | Passivity phenomenon

• The conc. nitric acid does not affect some metals e.g. (iron, chrome and aluminum). GR. Due to the oxidizing property of the acid; a non-porous layer of the metal oxide is formed which protects the metal from further reaction, what is known by passivity.

Passivity phenomenon

A non-porous layer of oxide is formed on the surface of the metal which protects it from further reaction with acids or atmospheric air.

Detection of nitrate ion NO_3^- (the brown ring experiment)

Steps:

- Add nitrate salt solution to a freshly prepared conc. solution of iron (II) sulphate in a test tube.
- Add carefully on the internal wall of the tube a few drops of conc. sulphuric acid.



Brown ring

Observation :

A brown ring appears at interface and disappears by shaking or heating.

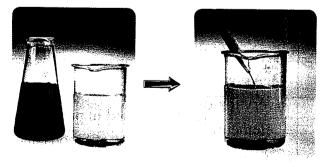
$$2\text{NaNO}_{3(\text{aq})} + 6\text{FeSO}_{4(\text{aq})} + 4\text{H}_2\text{SO}_{4(\ell)} \xrightarrow{\text{conc}} 3\text{Fe}_2(\text{SO}_4)_{3(\text{aq})} + \text{Na}_2\text{SO}_{4(\text{aq})} + 4\text{H}_2\text{O}_{(\ell)} + 2\text{NO}_{(g)}$$

$$\text{FeSO}_{4(\text{aq})} + \text{NO}_{(g)} \xrightarrow{\text{FeSO}_4.\text{NO}_{(s)}}$$
Brown ring compound

Differentiation between nitrite and nitrate salts

To differentiate between nitrite and nitrate salts, add to each solution of them a solution of potassium permanganate acidified with concentrated sulphuric acid if:

- The violet color of the permanganate disappears, the salt is nitrite.
- The violet color of the permanganate does not disappear, the salt is nitrate.



Nitrite solution removes the purple color of the permanganate

$$5 \text{KNO}_{2(\text{aq})} + 2 \text{KMnO}_{4(\text{aq})} + 3 \text{H}_2 \text{SO}_{4(\ell)} \xrightarrow{\text{conc}} 5 \text{KNO}_{3(\text{aq})} + \text{K}_2 \text{SO}_{4(\text{aq})} + 2 \text{MnSO}_{4(\text{aq})} + 3 \text{H}_2 \text{O}_{(\ell)}$$

Note

It is impossible to perform the flame test for elements of group 5A except (Arsenic As, Antimony Sb).

☆ The economic importance of the 5A group elements :

Element	Economic importance	
1. Nitrogen	 Manufacturing of: Ammonia gas. Nitrogenous fertilizers. Used in filling of car tires, as nitrogen reduces the probability of its explosion GR. Because it is not affected easily by changing of the temperature, in addition to its leakage rate is less than that of air. Used in filling chips packaging bags to keep potato's slices crunchy because it is relatively inactive. Liquified nitrogen is used in: Preserving and transferring the living cells and in treating some banging tumors. Manufacturing of: Matches. 	Fertilizes prinkler Filling car tires with nitrogen
2. Phosphorus	 Fire works. Phosphorus fertilizers. Many alloys such as phosphorus-bronze (Cu + Sn + P) which is used in manufacturing of p 	Matches oushing fans in ships.
3. Arsenic (very toxic element)	 It is used as a preservative substance for wood, due to its poisonous effect on insects, bacteria and fungi. It is used in preparing of arsenic trioxide compound which is used in treating of blood cancer. (Leukemia) 	
4. Antimony	 Manufacturing of: Lead antimonal alloy which is used in the acidified car batteries. Semiconductors technology which are used for manufacturing of instruments of detecting the infrared (IR) rays. 	
5. Bismuth	- Manufacturing of bismuth, lead and cadmium allog manufacturing of electric fuses and this is due to its	